REPORT SERIES IN AEROSOL SCIENCE
N:o 139 (2012)

NATURAL AND ANTHROPOGENIC INFLUENCES ON TROPOSPHERIC AEROSOL VARIABILITY

ARI ASMI

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation
To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in auditorium E204, Gustaf Hällströmin katu 2, on December 14th, 2012, at 12 o'clock noon.

Helsinki 2012

Author's Address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
e-mail ari.asmi@iki.fi

Supervisors: Academy Professor Markku Kulmala, Ph.D.
Department of Physics
University of Helsinki

Professor Veli-Matti Kerminen, Ph.D.
Department of Physics
University of Helsinki

Reviewers: Associate Professor Douglas Nilsson, Ph.D.
Department of Applied Environmental Science
Stockholm University, Sweden

Adjunct Professor Mikhail Sofiev, Ph.D.
Air quality research
Finnish Meteorological Institute

Opponent: Senior Scientist Andreas Maßling, Ph.D.
Department of Environmental Science
Faculty of Science and Technology
Aarhus University, Denmark

ISBN 978-952-5822-70-0 (printed version)
ISSN 0784-3496
Helsinki 2012
Unigrafia Oy

ISBN 978-952-5822-71-7 (pdf version)
http://ethesis.helsinki.fi
Helsinki 2012
Helsingin yliopiston verkkojulkaisut

Acknowledgements

I have worked with aerosols in one way or another since 1998. During this time, so many people have contributed in my work that it is completely impossible to thank everyone. I will thus only concentrate my thanks on some more recent collaborators, and even there just the most recently influential ones. The foremost person in this list is Acad. Prof. Markku Kulmala, who originally hired me in 1998 as a research assistant, and has been more or less directly my boss and/or supervisor ever since. His has had a major influence on my scientific career, from first studies with indoor aerosol modelling to project management during EUCAARI. He has also taught me not to give up easily[1], but also to cut the losses if needed[2]. My second supervisor and a good friend Prof. Veli-Matti Kerminen has been of extremely important help throughout my studies and scientific work. He has also corrected several issues with my bench press technique, which I will forever be grateful. I wish naturally to thank my pre-examiners, Adj. Prof. Mikhail Sofiev and Prof. Douglas Nilsson for their insightful and perceptive comments on this thesis.

For the scientific input besides my supervisors, the largest influence has been from my constant collaborator/co-worker/room mate Dr. Risto Makkonen, who did the boring part of the climate modelling, leaving the fun parts to me. He also had to listen my opinions on every subject related or unrelated to science. From my 60 co-authors in this thesis, I would like to especially mention Prof. Alfred Wiedensohler (IfT), Dr. Paolo Laj (CNRS), Prof. Ari Laaksonen (FMI), Dr. John Ogren (NOAA), and Dr. Martine Collaud Coen (MeteoSwiss), for their significant contributions in this work done.

I wish to thank all the staff in the Division of Atmospheric Sciences[3]. There are too many colleagues and friends to name individually, but perhaps I should mention the "old gang" of the old building cellar: Hanna, Ismo, Miikka, Tuukka, Pasi and Hannele.

I also want to acknowledge the funding agencies and institutions I have worked in: Maj and Tor Nessling foundation, Academy of Finland, Université Blaise Pascal – Clermont-Ferrand, Ford Motor Company, the European Commission and of course the Department of Physics in University of Helsinki. Their contributions has been very helpful.

There can not be many couples who argue in sauna about aerosol absorption properties. By quantity (and in some cases – quality), the highest amount of constructive criticism for this work has been from my lovely and loving wife, (Dr.) Eija Asmi. I do not think that without her I would have ever finished this work, at least in this form.

[1] Which is why this thesis has two columns.

[2] Which is why you, the reader, are holding this book.

[3] Although when I started there, it was Laboratory of Aerosol and Environmental Physics, located in the lowest cellar in the old institute building.

Ari Juhani Asmi
University of Helsinki, 2012

Abstract

Aerosol particles are everywhere in the atmosphere. They are a key factor in many important processes in the atmosphere, including cloud formation, scattering of incoming solar radiation and air chemistry. They have also been connected to adverse effects on human health and they have a strong effect on visibility. The aerosol particles have relatively short lifetimes in lower atmosphere, typically from days to weeks, and thus they have a high spatial and temporal variability. This thesis concentrates on the extent and reasons of sub-micron aerosol particle variability in the lower atmosphere, using both global atmospheric models and analysis of observational data.

Aerosol number size distributions in the lower atmosphere are affected strongly by the new particle formation from gaseous precursors, mostly organic vapours and sulphuric acid. Perhaps more importantly, a strong influence new particle formation is also evident in the cloud condensation nuclei (CCN) concentrations, suggesting a major role of the new particle formation in the climate system.

In this thesis, the sub-micron aerosol number size distributions in the European regional background air were characterized for the first time from consistent, homogenized and comparable datasets. The European background air is highly dominated by anthropogenic influences in Central Europe. In remote regions, such as Northern Europe, strong seasonal changes are consistent with a larger role of the biogenic sources suggested by earlier studies. The characterization work of European aerosols provides air quality and climate modellers unparalleled possibilities in model performance testing, and creates a basis for any regulatory efforts on sub-micron aerosol number concentrations.

Some recent studies have suggested that differences in aerosol emissions between weekdays could also affect the weather via aerosol-cloud interactions. These earlier studies of this "weekend-effect" were based on aerosol mass based proxies for CCN. In this thesis, the weekday-to-weekend variation of CCN sized aerosol number concentrations in Europe were found to be much smaller than expected from earlier studies. This suggests that any potential large scale "weekend-effect" of European meteorology is not directly influenced by CCN-sized aerosol particles, and some other explanation must be proposed. A key finding was also that aerosol mass or optical properties -based measurements are poor proxies for CCN concentrations in time scales comparable to aerosol particle lifetimes in the atmosphere. This result also suggests that a lack of weekday variability in meteorology is not necessarily a sign of weak aerosol-cloud interactions.

An analysis of statistically significant trends in past decades of measured aerosol number concentrations from Europe, North America, Pacific islands and Antarctica generally show decreases in concentrations. The analysis of these changes show that a potential explanation for the decreasing trends is the general reduction of anthropogenic emissions, especially SO_2, although a combination of several drivers for these changes in the number concentrations are likely.

The representative emission pathways developed for the IPCC prognose radical reductions of anthropogenic emissions in the next decades, especially of sulphur dioxide. This will most likely cause strong reduction in the present-day cooling effect of the atmospheric aerosols. The model simulations of this thesis show that effect will cause strong additional positive forcing on the atmosphere, possibly causing further increase in the near-surface mean temperatures. The effect was further magnified when new particle formation in atmosphere was also considered in the model calculations. Strong reductions in primary aerosol emissions and especially secondary aerosol precursors should be thus considered with caution.

Keywords: Atmospheric aerosol, Emission reductions, Weekend effect, New particle formation

CONTENTS

INTRODUCTION

This thesis consists of an introductory review, followed by 5 research articles. The introductory review consists of aims of the thesis, general properties of aerosols, introduction to and discussion on some of the aspects of the work described in the research articles and references.

In the introductory part, the research articles are cited with roman numerals:

PI Makkonen, R., **Asmi, A.**, Korhonen, H., Kokkola, H., Järvenoja, S., Räisänen, P., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., Järvinen, H., Lohmann, U., Bennartz, R., Feichter, J., and Kulmala, M. (2009). Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5–HAM global circulation model. *Atmospheric Chemistry and Physics*, 9(5):1747–1766.

PII **Asmi, A.**, Wiedensohler, A., Laj, P., Fjaeraa, A.-M., Sellegri, K., Birmili, W., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P., Hansson, H.-C., Fiebig, M., Kivekäs, N., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P. P., Swietlicki, E., Kristensson, A., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G., Henzing, B., Harrison, R. M., Beddows, D., O'Dowd, C., Jennings, S. G., Flentje, H., Weinhold, K., Meinhardt, F., Ries, L., and Kulmala, M. (2011). Number size distributions and seasonality of submicron particles in Europe 2008-2009. *Atmospheric Chemistry and Physics*, 11(11):5505–5538.

PIII **Asmi, A.** (2012). Weakness of the weekend effect in aerosol number concentrations. *Atmospheric Environment*, 11(11):5505–5538.

PIV **Asmi, A.**, Collaud Coen, M., Ogren, J. A., Andrews, E., Sheridan, P., Jefferson, A., Weingartner, E., Baltensperger, U., Bukowiecki, N., Lihavainen, H., Kivekäs, N., Asmi, E., Aalto, P. P. , Kulmala, M., Wiedensohler, A., Birmili, W., Hamed, A. , O'Dowd C. , Jennings, S.G., Weller, R., Flentje, H. , Fjaeraa, A. M., Fiebig, M., Myhre, C. L., Hallar, A. G. , and Laj, P. (2012). Aerosol decadal trends (II): In-situ aerosol particle number concentrations at GAW and ACTRIS stations. *Atmospheric Chemistry and Physics Discussions*, 12, 20849-20899

PV Makkonen., R, **Asmi, A.**, Kerminen, V.-M., Boy, M., Arneth, A., Hari, P., and Kulmala, M (2012). Air pollution control and decreasing new particle formation lead to strong climate warming *Atmospheric Chemistry and Physics*, 12(3):1515-1524.

Aims

The original aims of this work were connected to a common project with the Finnish Meteorological Institute and the University of Kuopio[4]. In the mid-2000s it became clear that the Finnish aerosol studies required a climate model to widen the perspective and get a hold on the complex feedbacks in the atmosphere, as models capable of including detailed aerosol microphysics started to become available. The Finnish aerosol and atmospheric groups started a co-operation with Max Planck Institute of Meteorology in Germany, for further development of ECHAM-HAM aerosol-climate model. This work resulted in the first paper (**PI**), which had the aim to **evaluate the sensitivity of CCN concentrations to new particle formation in a global context**.

In the work leading to this thesis, the results of **PI** directly lead to **PII**, when the quality of model comparison datasets became apparent (Fig. 1). Thus, a second aim was to **generate useful comparison datasets and metrics for large scale model simulations**. **PII** showed also a surprisingly weak weekday variation in CCN-sized aerosol particles. This result, together with my at-time interest in more advanced time-series analysis, led to a study with the main aim to **characterize this weekly variation in more detail and to provide theoretical background for the visibility of oscillations over background noise**.

The **PV** were a result of **PI**, in the sense that we needed to know at least the pre-industrial conditions on our model version to get any idea of the anthropogenic aerosol influence on the climate. This was nicely collaborated by IPCC WG1 asking for a trend analysis on the past decades aerosol measurements. As I had some experience on aerosol number concentration data analysis, and it well supported the **PV** aims, I decided to volunteer as (co)investigator on the subject (**PIV**) with the aim to **evaluate the changes on aerosol number concentrations in the last decades based on experimental data**. The modelling studies of past, present and future had the aims to **characterize the anthropogenic influence on ECHAM5-HAM with nucleation mechanisms included** and to **study the changes in the climate forcing of aerosols from IPCC emission pathways**.

[4] nowadays, University of Eastern Finland

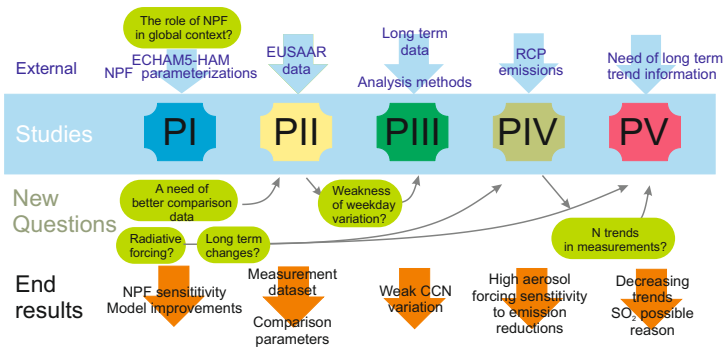

Fig. 1: A simplified summary of connections between the studies of this thesis.

1. GENERAL PROPERTIES OF ATMOSPHERIC AEROSOLS

The terrestrial atmosphere is a mixture of nitrogen, oxygen and argon with small amount of trace compounds (Lide, 2004). A good whiskey is a mixture of water and ethyl alcohol with a small amount trace compounds (Pryde *et al.*, 2011). In both cases, even though both have major and important active compounds (oxygen and alcohol respectively), the interesting part[1] are the minor constituents. The impurities and trace elements matter, and they are as critical to the behaviour of the atmosphere, as they are for the taste of a good single malt. In atmosphere, the impurities include components such as carbon dioxide, liquid water droplets (commonly observed as clouds) and, among many others, aerosol particles.

1.1 Aerosol phases

Aerosols, in contrast to other atmospheric impurities, are a phase mixture. By definition, an aerosol consists of two parts: the gas phase (air and other gasses and vapours) and the particle phase (liquid, solid or multiphase particles). The gas phase fraction of the atmospheric aerosol can be thought to consist of essentially inert carrier gas and a selection of potentially condensing vapours, precursor gases, oxidants and other reactive gaseous species. The particle phase consists of a relatively low number of particles of varying size and composition in a constant interaction with the gas phase. The aerosol can be affected by external forces, such as radiation, temperature gradients and other physical processes, changing the environment in the phase mixture. These changes can then facilitate phase changes and chemical processes, affecting the properties of the aerosol.

1.2 Aerosol particle size and composition

Individual aerosol particles are in atmospheric science usually characterized mostly by their size and composition (Seinfeld and Pandis, 2006). The particle size is usually determined by the representative particle diameter, d_p, which can vary in atmospheric aerosol particles from around one nanometre to approximately hundred micrometres. Figures 2a-b show examples of aerosol particle sizes in comparison to wavelengths of electromagnetic radiation and some biological entities. The particle population in a macroscopic volume of air is commonly referred as **aerosol size distribution** for some aerosol property as a function of particle size. Figure 2b shows some examples of the aerosol particle number size distribution function, with a customary $dN(d_p)/d\log_{10} d_p$ normalization[2]. Several wide peaks are typically visible in the

[1] Admittedly depending on the person.

[2] This normalization is far from the only possible, normalizations with natural logarithm $dX(d_p)/d\log_e d_p$ and linear size range $dX(d_p)/d_p$ are also used in literature. The normalization is

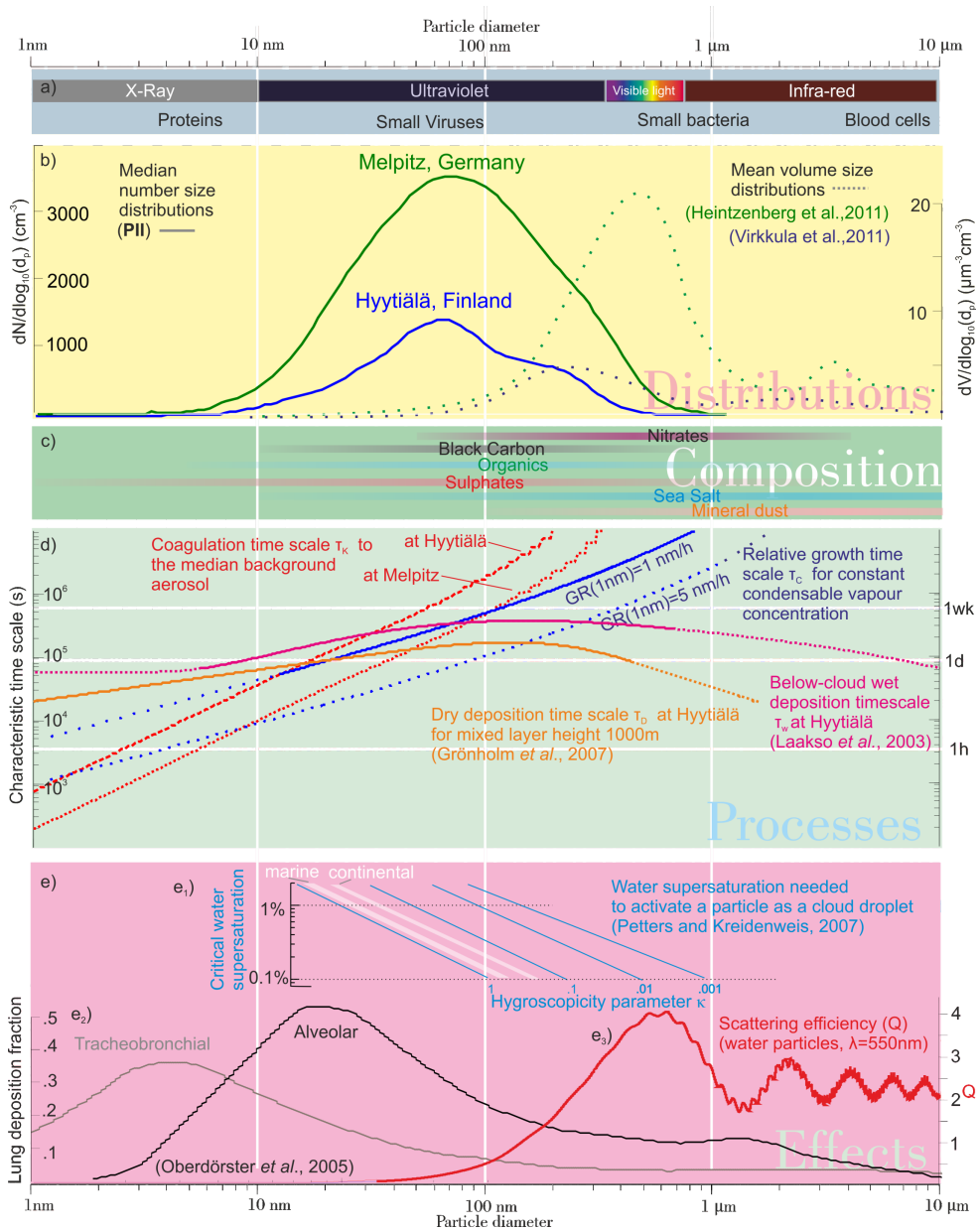

Fig. 2: Composite picture of (a) comparable length scales of electomagnetic radiation wavelengths and some biological entities, (b) typical atmospheric aerosol particle number and mass size distributions, (c) typical species in continental aerosol, (d) aerosol microphysical processes converted to characteristic time scales, and (e) processes important to aerosol climate (e_1, e_3) and health effects (e_2) as a function of particle dry diameter. Mie calculations of scattering efficiency are courtesy of Mr. John Backman (U. Helsinki).

size distributions, indicating aerosol populations, or modes. These represent persistent aerosol populations are often found in the atmosphere as a result of particle sources, sinks, and mixing and growth processes. Commonly, the atmospheric submicron ($d_p < 1\mu m$) aerosol number size distributions have an Aitken mode (diameters around 30 to 100 nm) and an accumulation mode (from 100 nm to 1 μm) separated by the so-called Hoppel gap (Hoppel *et al.*, 1990). This gap is more prominent in remote locations, and for example the data shown for Melpitz, Germany, have very little indication of such modal difference in the median aerosol number size distribution. This gap is most likely a result of cloud processing of aerosols, and is thus indicative of aerosol size distribution history. Sometimes the nucleation mode (below 30 nm) is visible, as are parts of the mostly super micron coarse mode. As a comparison, the mean volume size distributions, which are indicative of the aerosol mass distributions, are much more concentrated on the larger particle sizes. This shift is a natural result of the d_p^3 scaling between the two aerosol properties, and shows that the majority of aerosol number concentration is concentrated in the smaller half of the submicron range; the majority of aerosol mass is concentrated in the over 100 nm diameter particles. Typical European background of aerosol particle number size distributions are discussed in length in **PII**.

By total mass, a considerable fraction of ambient sub-micron tropospheric atmospheric aerosol particles are composed of water (Wang *et al.*, 2008; Ervens *et al.*, 2011). The remaining mass of the submicron aerosol in the continental troposphere consists of sulphates, nitrates, organic compounds, ammonia and black carbon, with contributions from mineral dust and sea salt (Figure 2c and e.g. Putaud *et al.*, 2004). The super-micron aerosol is usually more dominated by the mineral dust and sea salt. The spatial variation in the aerosol composition illustrates the source areas of different types of particles (Figure 3). The particle composition is also dependent on the particle age in the atmosphere, as more and more condensible matter, especially sulphates and organics, condense on the particles or are produced by cloud processing or heterogeneous reactions. Freshly-emitted particles form external mixtures with pre-existing particles, where the aerosol particles of the same size have different compositions. Ageing processes, such as condensation and evaporation, reduce these differences until the population starts to be more uniform, with different compounds internally mixed in the particles. In the real atmosphere, the aerosol is a complex mixture of both kinds of aerosol mixing types, although the time-scales for change e.g. from freshly emitted hydrophobic combustion particles to more hygroscopic internal mixtures is often rather short, of the order of hours (Ervens *et al.*, 2010; Riemer *et al.*, 2010).

The particles in the atmosphere have a multitude of sources. Sulphates are mostly from anthropogenic emissions, volcanoes, marine Dimethyl Sulphide (DMS) emissions, and from subsequent photochemistry and cloud processing. Ammonium and nitrates are generated by biological processes and fertilizers, oceans can also be a significant source of ammonium; Black carbon (i.e. strongly absorbing aerosol) comes from combustion sources (including biomass burning); organics come from the vegetation, anthropogenic sources, biomass burning and oceans; and dust and sea salt

used, as it makes the size distributions measured with differing size resolution more comparable, and if the size axis is given in logarithmic scale, the area under curve normalised with logarithm of diameter is proportional to the total aerosol number concentration. The particle size d_p inside the logarithm is assumed to be divided by the length unit used.

come from deserts and oceans, respectively.

The sources of atmospheric particle are generally divided into two categories: primary and secondary. Primary sources generate aerosol particles directly to air, e.g. in the case of atmospheric dust from resuspension over deserts, organics and sea salt particles from evaporation of sea water droplets (bubble bursting) and spuming, or carbon aggregates from diesel combustion. Secondary particles are formed from gas phase compounds in the atmosphere via new particle formation. In some cases, the division is more difficult as the division between the two kinds of particles is up to the scale which the emission is characterized: sulphate particles from combustion could be either considered direct emissions when measured far from the source, or secondary, if measured directly from exhaust. The division between primary and secondary aerosol is further complicated by terminological issues. In many studies the primary/secondary split is done for aerosol mass, not by particles *per se*. In these cases, the primary aerosol (mass) is directly emitted and secondary consist of all mass condensed or otherwise produced to aerosol particles after emission. This separation is especially relevant for the discussion of Secondary Organic and Secondary Inorganic Aerosol (SOA and SIA) in papers **PI** and **PV**.

Of particular note in aerosol particle composition are the two main species or species groups discussed in **PI** and **PV**, sulphuric acid (H_2SO_4) and organic compounds. The sulphuric acid is often considered to be the key species in atmospheric new particle formation, due its general availability as a photo-oxidation product of SO_2, simplified oxidation pathway and the extremely low value of saturation vapour pressure. These properties make the sulphuric acid very keen on either condensing to existing surfaces (including particles), or if no such surface is available, to take part in new particle formation. A close correlation between H_2SO_4 and new particle formation in troposphere is evident from field data (e.g. Weber *et al.*, 1996; Kuang *et al.*, 2008; Nieminen *et al.*, 2009; Paasonen *et al.*, 2010), also seen in chamber experiments (Sipilä *et al.*, 2010; Kirkby *et al.*, 2011). In particles, sulphuric acid reacts to form sulphates.

The second particularly interesting group of species are the organic compounds. The importance of organic compounds come from the fact that they are a major part of aerosol particle composition in the submicron range (Jimenez *et al.*, 2009), can affect the aerosol-cloud interactions and aerosol optical properties (Facchini *et al.*, 1999; Ramanathan *et al.*, 2005; Andreae and Gelencsér, 2006; Prisle *et al.*, 2012), are critical on aerosol growth to cloud condensation nuclei (Kerminen *et al.*, 2000, 2012), and that measured concentrations are generally poorly reproduced in the atmospheric models (Kanakidou *et al.*, 2005). There are figuratively innumerable different organic compounds in the ambient atmospheric aerosol, and thus usually some lumping method is used to categorize them. The current approaches in the literature are based often on chemical characterization methods of particles (e.g. Decesari *et al.*, 2000; McFiggans *et al.*, 2010), their saturation vapour pressure (e.g. Donahue *et al.*, 2006, 2012), oxidation state (Kroll *et al.*, 2011), or semi-empirical smog chamber partitioning properties (e.g. Odum *et al.*, 1997). Due the high complexity of organic chemistry and lack of suitable data, the handling of organic compounds is still very uncertain in aerosol models. However, the current advances in the measurements of aerosol chemistry provide a good basis for improved parametrizations of processes connected to at least the most relevant organic compound classes.

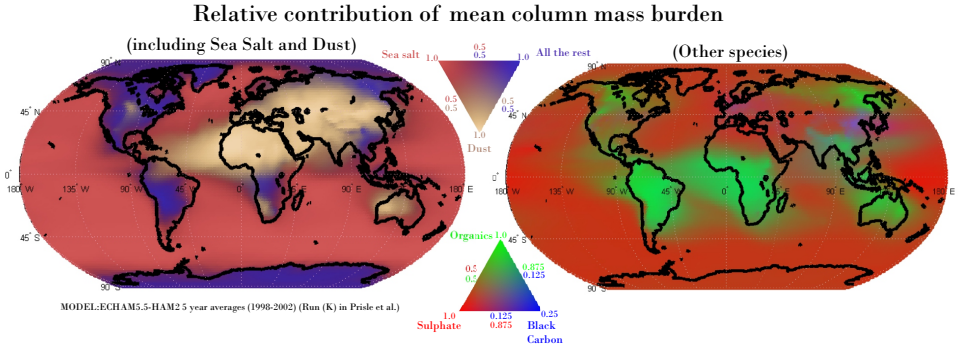

Fig. 3: Example of relative mean contribution of different aerosol composition species to column mass burden (ECHAM5-HAM2 simulations analyzed for Prisle *et al.* (2012)). The left figure shows the contribution of mainly coarse mode species (sea salt and dust) in comparison to all other species, and the right figure shows the relative contribution of the rest of the simulated species. ECHAM5-HAM2 lacks nitrates and ammonia, and the column burdens are given without water in the particles. Note that scale for black carbon is different from the other species' scales.

1.3 Processes

As the particle lifetimes vary from seconds to a few weeks, their variability in the atmosphere is much greater than of many long-lived gaseous pollutants, leading to spatially and temporally inhomogeneous aerosol concentrations (Jaenicke, 2008). Variations in available radiation, clouds and oxidants transform and age the aerosol populations in atmosphere (Seinfeld and Pandis, 2006). The atmospheric aerosol populations are thus in a constant state of change.

The huge range of particle sizes (altogether around 5 orders of magnitude in diameter) is also mirrored by the variability of strength of different microphysical processes affecting the particles. Figure 2d shows characteristic time scales of some of the processes in typical boundary layer conditions.

The smallest particles are very sensitive to removal by collision to larger aerosol particles via **Brownian coagulation**, with the characteristic time scale of

$$\tau_K(d_p) = \frac{1}{\int_{\mathrm{d_p}}^{\infty} K(d_p, d_{pb}) N_b(d_{pb}) dd_{pb}}, \tag{1.1}$$

where K is the Brownian coagulation coefficient ($\mathrm{cm^3 s^{-1}}$), and N_b is the background aerosol number distribution ($\mathrm{cm^{-3}}$). This process also grows the larger particles, although the effect is generally relatively minor due the large volume differences between the particles. As the particle size increases, the coagulation efficiency decreases rapidly, shown as the increase of the characteristic time scales in Figure 2d.

Particles can be removed also by sticking to existing surfaces by **dry deposition**, which is relatively efficient for particles outside of Aitken and accumulation mode ranges, but only in atmospheric layers near to the ground. For a well mixed boundary layer, the characteristic dry deposition time scale $\tau_d(d_p)$ could be defined as

$$\tau_d(d_p) = \frac{H}{v_d(d_p)} \tag{1.2}$$

where v_d is the (particle and environment

dependent) dry deposition velocity (ms^{-1}) and H (m) is the mixed layer height. The dry deposition characteristic time shown in Figure 2d is for 1000 m mixing layer height and based on the v_d observations in in Hyytiälä; different environments and different meteorological situations can significantly change the dry deposition rates, and even the shape of the particle size dependence (Pryor *et al.*, 2008). Aerosol particles can also be removed from the atmosphere by falling raindrops or snow (**below-cloud scavenging**), by being activated to cloud droplets and precipitating (**activation scavenging**) or by colliding with cloud droplets (**in-cloud scavenging**). The time scales of these processes are even harder to determine, as they are strongly related to cloudiness, precipitation frequency and rain droplet sizes. The issue is even further complicated by the fact that most particles activated as cloud droplets usually evaporate when leaving the cloud and do not precipitate. The below-cloud scavenging is only efficient for small or large particles ($\mathrm{d_p} < 100\mathrm{nm}$ or $\mathrm{d_p} > 1\mu\mathrm{m}$, Pruppacher and Klett (1997)), and only relatively large particles ($\mathrm{d_p} > 50\mathrm{nm}$) can activate as cloud droplets (see next section on cloud condensation nuclei). A rough indication of below cloud wet deposition time scales $\tau_w(d_p)$ can be estimated from

$$\tau_w(d_p) = \frac{t_0}{\sum_p f(p)\left(1 - \exp(-\Lambda(p, d_p)t_0)\right)}, \tag{1.3}$$

where p is accumulated precipitation (m) in collection time t_0, $f(p)$ is the fraction of time with p binned precipitation accumulation and Λ is the below cloud scavenging efficiency. The time scales the Figure 2d are produced using t_0 of 30 minutes, precipitation accumulation $f(p)$ from Hyytiälä forestry station (Months V-IX, 2000-2005) and Λ from Laakso *et al.* (2003).

Particle interactions with the gas phase are crucial to aerosol population dynamics. Oxidation of vapours and gases create low-volatility compounds, which can condense on existing particles (**condensation**) and in some cases even form new particles (**nucleation**). The rates of condensation on particles are strongly dependent on the particle size and on concentrations of condensible vapours. In Figure 2d, the condensation time-scales are shown for a zero vapour pressure model compound, with a constant concentration. The concentration levels are normalized by the growth rate ($\mathrm{GR} = \mathrm{dd_p/dt}$) which such concentration would generate for a 1 nm particle ($\mathrm{GR_{|1nm}}$). In this case, the characteristic time scale[3] would then be

$$\tau_C(d_p) = \frac{d_p}{GR(d_p)}, \tag{1.4}$$

and the used values of $\mathrm{GR_{|1nm}}$ are comparable for observed growth rates during new particle formation in Hyytiälä (Yli-Juuti *et al.*, 2011). In the real atmosphere, the concentrations of condensible vapours are very rarely constant, and thus the condensation growth will vary in time. The smallest particles (generally diameters less than 10 nm) could also be affected by the Kelvin effect in respect to organic vapour condensation, reducing the condensation rate (Kulmala *et al.*, 2004d), although this process is not included in the Figure 2d. The semi-volatile species, such as some organic compounds, can also evaporate from the particles (Robinson *et al.*, 2007). Chemistry, environmental changes, particle internal partitioning and meteorology can strongly affect the particle/gas phase processes. For example, an important global source of accumulation mode mass is **cloud processing**, where activated cloud droplets scavenge pollutants from air, which after aqueous phase chemistry and cloud evap-

[3] The definition of condensation time scale here is for relative change rate of diameter and is slightly different from volume change rate used in e.g. Raes *et al.* (2000).

oration remain in the particles (Yin *et al.*, 2002). This is a major source of sulphate and organic compounds in the CCN-sized particles and explain a great deal of particle growth from Aitken to accumulation modes (Kerminen and Wexler, 1995; Ervens *et al.*, 2011).

The lifetimes of atmospheric aerosol particles are generally smaller than many other climate-impacting impurities (Jaenicke, 2008). The lifetimes are, however, very strongly dependent on the particle size and environmental factors. Fast coagulation of small (d_p<20 nm) particles lead to short lifetimes due to their rapid coagulation with larger particles. Larger particles (in forest environments, d_p>200 nm) are removed efficiently via wet or dry deposition. The condensation is relatively efficient up to Aitken mode particles. For the larger particles the cloud processing or heterogenous reactions are more efficient growth processes. The lifetimes of the particles are generally longer in greater altitudes of the atmosphere, but still very short compared to e.g. methane or carbon dioxide. This means that spatial and temporal variability of aerosol particles is much higher than many other climate impacting impurities, and the changes in emissions are rapidly seen in the overall concentration levels.

1.4 Impacts

Atmospheric aerosols affect the atmosphere in many ways. These impacts are the key motivation behind studies of atmospheric aerosols. This thesis is mostly about the aerosol effects on weather and climate, and to less extent, on human health. The aerosol particle size dependency of some of these the impacts are summarized in Figure 2e.

1.4.1 Climate impacts

Aerosols are affecting the climate system in many important ways. The most obvious of these is the scattering and absorption of incoming solar radiation before reaching the surface. These **direct aerosol effects** can either cool or warm the atmosphere, and change the atmospheric circulation. These changes in the atmosphere can also cause complex changes in the clouds (**semi-direct effects**, Koch and Del Genio, 2010). The absorbing aerosol generally warm the atmosphere by absorbing incoming solar radiation, dependent on the amount of absorbing material in the particles (Ångström, 1929). The extinction of solar radiation from scattering to aerosol particles is related to particle surface area, and refractive index-dependent scattering efficiency Q. Figure $2e_3$ shows the scattering efficiency of pure water particles in 550 nm radiation. Although the shape of the scattering efficiency function depends on particle properties, generally only particles larger than approximately 100 nm diameter have a strong contribution to direct light scattering in the atmosphere.

In this thesis the main interest is in the **indirect effects** of aerosols through clouds. The two most studied indirect effects[4] are presented schematically in Figure 4. The cloud-albedo (Twomey) effect, is based on the elevated aerosol number concentrations increasing the number of cloud droplets in clouds, generating whiter (higher albedo)

[4] There are a number of other proposed mechanisms of aerosol indirect effects, based on aerosol affecting the entrainment of dry air to the clouds and thus cloud water content or albedo: Drizzle-entrainment effect (Lu and Seinfeld, 2005), sedimentation-entrainment effect (Ackerman *et al.*, 2004) and evaporation-entrainment effect (Wang *et al.*, 2003). However, even though these processes have been studied in small scale Large Eddy Simulations (Chen *et al.*, 2011), I am not aware of any parametrizations for global scale models, and thus global impacts of these processes are still very uncertain.

clouds and thus reflecting more solar radiation (Twomey, 1977). The cloud lifetime (Albrecht) effect is based on smaller cloud droplets having less chance to generate rain, increasing cloud lifetime and thus cloudiness (Albrecht, 1989). These effects are mostly dependent on the ability of some aerosol particles to act as a seed for the cloud droplet formation, i.e. act as Cloud Condensation Nuclei (CCN).

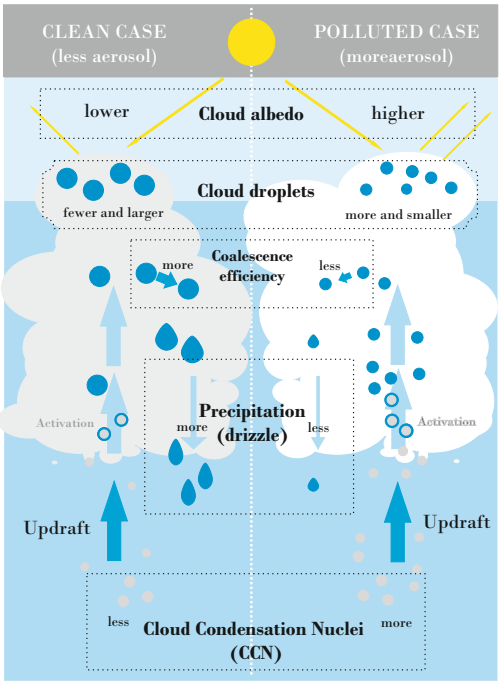

Fig. 4: Simplified schematic of cloud albedo (Twomey) effect and cloud lifetime (Albrecht) effects, as a change of cloud properties between clean (left) and polluted (right) environments.

Cloud condensation nuclei

Cloud condensation nuclei are a commonly used term for particles on which cloud droplets can be formed in cooling air parcels in the atmosphere. Many of the aerosol-cloud interactions are related to the number of available CCN, and thus much of the research in this thesis is one way or another connected with determining some property related to CCN. The ability of an aerosol particle to activate as a cloud droplet depends on the particle properties (size, hygroscopicity, presence of surfactants) and on the meteorological situation (updraft velocity, water vapour, temperature). Of these properties, the particle size is commonly considered to be of greater importance than composition (Dusek *et al.*, 2006; McFiggans *et al.*, 2006), and the meteorological situation is typically represented only by the critical water supersaturation at the moment of cloud activation. This approach was used in the **PIII**, where direct measurements of $CCN_{.4\%}$ (i.e. aerosol particles activated at water saturation of 1.004) were available. However, long-term measurements of CCN are not very common. The instruments for measuring them have only recently became stable enough for monitoring use (Nenes *et al.*, 2001; Sihto *et al.*, 2011), and thus other methods to derive CCN concentration need to be used. In **PII**, **PIII** and **PIV**, the CCN concentration was approximated from size distribution data, using a fixed cut-off diameter to produce different **CCN proxies**. This simplification is based on the assumption of relatively low importance of particle chemistry in the CCN activation.

In many modern studies, the aerosol composition effects are described by a simplified one-parameter approach. This approach, developed by Petters and Kreidenweis (2007), describes all composition effects on particle hygroscopicity, and thus on the cloud activation, with the so-called κ

parameter. Low values of κ are connected with a low hygroscopicity, i.e. particles which require higher water supersaturations to activate as cloud droplets in comparison to high κ particles. Figure 2e$_1$ shows the effect of this parameter on cloud activation potential via showing the critical water supersaturation needed to activate particles as cloud droplets as a function of κ and d_p. As the particles age in the atmosphere, they start to have more and more uniform κ values, close κ values of 0.3±0.1 for continental and 0.7±0.2 for marine aerosol (shown as a white shaded areas in Fig. 2e$_1$, Andreae and Rosenfeld (2008)). This relatively small variation in ambient κ values support the use of aerosol diameter -based CCN proxies, although the cloud properties and updraft velocity still play a strong role in potential CCN activity.

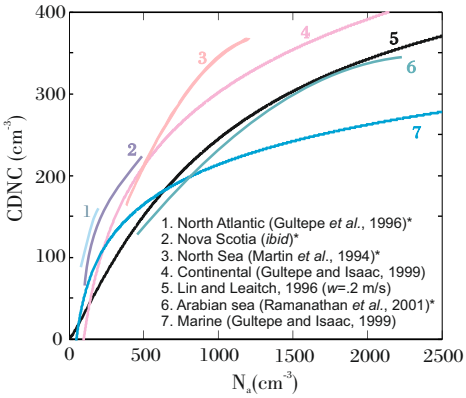

Fig. 5: Published semi-empirical relationships between "CCN-sized" aerosol number concentrations (N_a) and cloud droplet number concentrations. Different studies used different size ranges for their definition of CCN, commonly close to 70-100 nm in diameter. *) Adapted from Ramanathan *et al.* (2001a).

The relationship between below-cloud CCN and cloud droplet number concentrations are not linear, and several methods for approximating the cloud activation have been proposed. The semi-empirical approaches, in contrast to mechanistic methods, have the advantages of having large enough scale of measurements to be comparable with climate model grid boxes, being easy to implement, and describing an actual measured cloud activation (Gultepe and Isaac, 1999). The generalization of such parametrizations to different environments can be difficult. Different clouds can have different updraft velocities, entrainment rates and water contents, and the aerosol properties, beyond a simple number concentration over selected activation diameter, are not taken into account. Still, the different semi-empirical parametrizations give relatively similar behaviour, with decreasing response to higher CCN concentrations, approximately related to the logarithm or fractional power of the CCN concentration (Figure 5). Notably, the parametrization by Lin and Leaitch (1997), taking into account both CCN (defined as particle number concentration above 70 nm in diameter, N_{70}) and model estimated cloud updraft velocity, was used in Global Circulation Model (GCM) simulations of this thesis (**PI** and **PV**). Some models can also use mechanistic methods for the cloud activation (Ghan *et al.*, 2011, for a review of recent parametrizations). The mechanistic methods give possibility to include many additional processes into the CCN-to-CDNC processing, making possible to study effects of e.g. changes in aerosol composition or co-condensing species (Makkonen *et al.*, 2012; Prisle *et al.*, 2012).

1.4.2 Health effects

Atmospheric aerosols (or, in air-quality terms *particulate pollution*) also affect human health. A classical example of the dangerousness of anthropogenic particulate pollution was observed in extreme pollution events in London 1952, where a strong photo-chemical particulate pollution cloud covered the city and caused excess mortality of approximately 12,000 in the metropolitan area(Brimblecombe, 1987; Bell *et al.*, 2004). More recently (from 1970s on) studies have clearly connected aerosol mass concentrations (particulate matter, PM[5]) to general health of the population, especially to lung cancer and cardiovascular mortality (Dockery *et al.*, 1993; Dockery and Pope, 1994), thus creating a strong epidemiological basis for the air quality standards of particulate mass (Pope, 2000).

Nanoparticles ($d_p < 100$ nm) have been widely acknowledged to have the potential for adverse health effects (Donaldson *et al.*, 1998, 2002; Sager and Castranova, 2009). The particle deposition to alveolar region of lungs can be especially efficient for particles of diameters below 50 nm (Figure 2e$_2$ and Oberdörster *et al.* (2005)). This is important, as such particles do not have any measurable effect on particle mass concentrations (Fig. 2b), and are thus not monitored in common air quality networks, nor regulated by legislation. However, there is no consensus on which aerosol property (e.g. size, composition, surface area) has strongest effect on human health (Wittmaack, 2007, and associated online correspondence). The different behaviour of PM and nano-particles in the atmosphere are discussed in **PIII**.

[5] The normal measure of particulate matter is PM_x concentrations, which are the particle mass below some pre-defined size limit. In health studies and air quality monitoring the most common measures are PM_{10} and $PM_{2.5}$, i.e. particle mass below 10 or 2.5 micrometer aerodynamic diameter.

2. SMALL PARTICLES – GLOBAL CONSEQUENCES

Gas phase oxidation results in generation of very low volatility compounds, which can, in absence of suitable condensation surface, create new particles in the atmosphere. This process has been detected frequently all over the continental planetary boundary layer (Kulmala *et al.*, 2004a). Unfortunately, no clear consensus which are the actual processes dominating this phenomena has yet emerged. Another issue is how significant such process can be in the atmosphere. The only comprehensive way to approach this problem is to use a global model capable of simulating both aerosol processes and the behaviour of the surrounding atmosphere.

2.1 New particle formation

One of the major sources of particle number concentrations is the gas-to-particle conversion, or nucleation. The process of new particle formation (NPF) in the atmosphere is complex, and many studies have proposed mechanisms to explain this phenomena in the atmosphere. Some proposed mechanisms for the initial atmospheric nucleation are binary H_2SO_4-H_2O (e.g. Vehkamäki *et al.*, 2002) or ternary H_2SO_4-H_2O-[base] (e.g. Napari *et al.*, 2002; Bonn *et al.*, 2008; Kurtén *et al.*, 2008) processes, sometimes including ion-induced effects (e.g. Yu and Turco, 2000; Lovejoy *et al.*, 2004). There is no reason to assume that all atmospheric nucleation is from the same mechanism, and some (or none) of these processes could be active in different environments. One should distinguish the actual initial formation of the particle (nucleation) from the subsequent growth/removal competition, resulting in observable particle formation[1]. In this sense, the inclusion of organic vapours can be critical for the newly nucleated particles (slightly above 1 nm in size) to survive to more detectable sizes, even though they might not actually nucleate themselves (e.g. Anttila and Kerminen, 2003; Kulmala *et al.*, 2004b).

Different semi-empirical approaches have also been suggested for NPF using either laboratory approaches (e.g. Hanson and Lovejoy, 2006) or field observations (e.g. Sihto *et al.*, 2006; Paasonen *et al.*, 2010, 2012). In **PI** and **PV**, simple parametrizations of the NPF rate were used in the form

$$J_n = C[\mathrm{H_2SO_4}]^k, \tag{2.1}$$

where J_n is the nucleation rate ($\mathrm{cm^{-3}s^{-1}}$), C is an experimentally determined prefactor ($(\mathrm{cm^3})^{\mathrm{k-1}}\mathrm{s^{-1}}$), k is experimental fitting parameter and the H_2SO_4 concentration is given in molecules per cubic centimetre (Sihto *et al.*, 2006). In case of $k = 1$, Equation 2.1 describes a process called activation nucleation, and with $k = 2$ it is called kinetic nucleation. Naturally, the pa-

[1] This difference is nowadays getting smaller and smaller, as detection limit of instruments is already at or close the diameters particles are forming (Vanhanen *et al.*, 2011).

rameters C and k include a lot of information on background physics and chemistry (e.g. concentrations of condensible organic vapours), and as such the overall applicability of one fitting to other locations is not certain. When **PI** was written, no better information was available, and the study should be considered to be a sensitivity study of these processes. In **PV**, this nucleation method was only used over land areas. More recently, parametrizations including a factor depending on the amount of condensible organic vapours have been developed (Paasonen *et al.*, 2010, 2012).

2.1.1 Life and death of a new particle

The nucleation mechanism is just a part of the actual new particle formation event. Right after formation, the new particles are extremely small, and thus have high potential to coagulate with existing particles. The only way for them to grow to the relative safety of Aitken mode sizes is either by condensational growth or by heterogeneous processes, helped by e.g. salt formation or oligomerization (Riipinen *et al.*, 2012). This competition between coagulation and growth processes is extremely important for the observable new particle formation rates, and determines often the actual total and CCN number concentration with at least as importantly as the actual nucleation rates and mechanisms (Kulmala *et al.*, 2004b; McMurry *et al.*, 2005; Pierce and Adams, 2007). Figure 6 illustrates the importance of condensation and coagulation processes, as the surviving fraction of newly nucleated particles is a strong function of both background aerosol concentration and the mean growth rate of the particles.

2.2 Global climate model ECHAM5-HAM

Aerosol formation, and especially the interaction with aerosols and atmosphere, has many complex feedbacks. The necessary parameters of aerosol formation and growth are determined by the climate system, which via aerosol-climate effects, is also affected by the changes in aerosol fields themselves. This kind of complex feedbacks requires a specific kind of model to study: a climate model with an aerosol microphysics module.

PI and **PV** used the ECHAM5-HAM General Circulation Model (GCM) to study aerosol-climate interactions. ECHAM5-HAM was one of the first models to include all of the micro-physical aerosol processes (Chapter 1) in a consistent GCM framework (Stier *et al.*, 2005). This is significant improvement from most other GCMs, which still use either prescribed aerosol fields, or simplified aerosol mass-based mechanisms (Textor *et al.*, 2007). The need for detailed aerosol processes is especially relevant for the studies of new particle formation, as NPF is strongly influenced by changes in the aerosol size distribution and related chemistry.

The base ECHAM5 model is a spectral global general circulation model, i.e. the primitive equations are solved in Fourier space, which is then in each time-step converted back to Eulerian grid for other (including aerosol and cloud) processes (Roeckner *et al.*, 2003). The model resolution used in **PI** and **PV** was T42, which correspond to approximately 2.8x2.8° in horizontal resolution, and around 300 km grid spacing at the Equator. The vertical levels of the model are defined by 19 (**PI**) or 31 (**PV**) terrain following hybrid-σ levels up to 10 hPa. As a general circulation model, it can generate a relatively realistic repre-

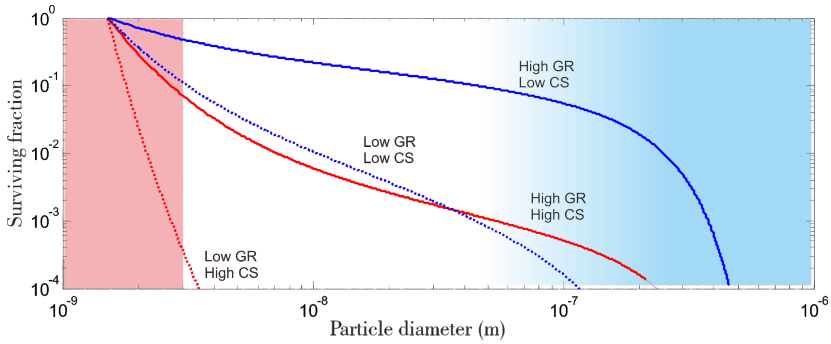

Fig. 6: "Surviving fraction", i.e. how much of particles nucleated in 1.7 nm diameter are still left in larger diameters after growth and loss processes, in different idealised background conditions. "High GR" describes situation with constant concentration of condensible vapour, normalized to give 5 nm/h growth rate for 1 nm particles. "Low GR" same with 1 nm/h growth rate for 1 nm particles. "High CS" corresponds to coagulation sink calculated from Melpitz and "Low CS" to Hyytiälä median aerosol number distribution (see Figure 2b). The Kelvin effect is not included in the calculations. Red area shows the region where the Kerminen and Kulmala (2002) parametrization (eq. 2.2) was used in **PI** and **PV**, blue are where the aerosol particles start to either act as CCN or efficiently scatter solar radiation.

sentation of a climate system, including advection patterns, radiation, clouds and precipitation. What it can not do, however, is a realistic representation of weather. This is important when considering potential comparison parameters from atmospheric measurements. discrepancy always remains.

The aerosol module HAM (Stier *et al.*, 2005) is based on modal description of the aerosol size spectrum, with aerosol dynamics from M7 submodule (Vignati *et al.*, 2004). For computational reasons, the aerosol mass and number size distributions are described by a set of 7 log-normal aerosol modes (Figure 7). The different modes have limited set of properties and species, concentrating the species tracers in the most likely modes where they could be present. One constrain is that the modes have fixed standard deviations, and they are limited in the size space, forcing the aerosol size distribution to always have exactly 7 modes in predetermined order. The M7 approach also includes tracers for external mixing, in the form of non-soluble modes in Aitken and accumulation modes. Although computationally efficient[2], and often quite good representation of overall aerosol population, the modal approaches do suffer some drawbacks, of which the most relevant to NPF studies, is the requirement of log-normality.

The nucleation processes create high concentrations of particles in extremely small sizes below 3 nm diameter. The rapid nucleation and subsequent growth and coagulation processes of sub-3nm particles make their modelling difficult using a single lognormal mode, especially considering the model chemistry time step of 30 minutes.

[2] Efficient in comparison to some other size distribution descriptions. Including the aerosol tracers for HAM result in a major additional computational overhead in comparison to standard ECHAM GCM. This is one of the reasons why ECHAM-HAM is not used in long Earth System model simulations for Intergovernmental Panel for Climate Chance (IPCC) Fifth Assessment Report (AR5) long-term Earth System simulations.

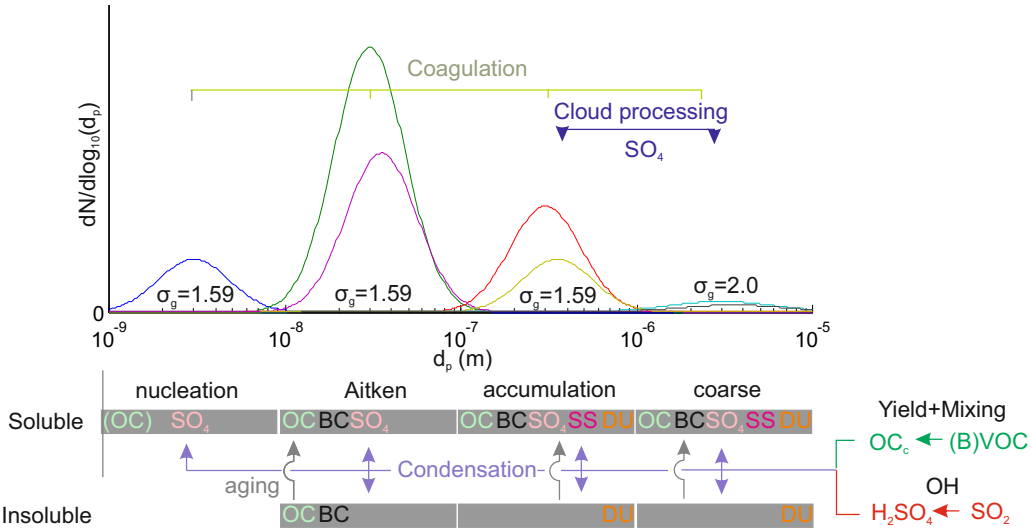

Fig. 7: Simplified description of M7 aerosol dynamics submodel of ECHAM5-HAM used in **PI** and **PV** (Vignati *et al.*, 2004). The model describes the aerosol size distribution with 7 lognormal models (4 soluble and 3 insoluble), and follows both number concentration of the modes and mass concentrations of different species in the modes (OC=organic carbon, SO_4=sulphate, BC = black carbon, SS = sea salt, DU = mineral dust). Modes which grow (or shrink) towards model boundary will have part of their mass and number transferred to neighbouring mode, thus keeping the modal structure relatively rigid. Particles in insoluble modes are transferred to soluble modes via coagulation and condensation ("aging" in the figure). Organic tracer in nucleation mode, and possibility of SOA forming via BVOC oxidation are **PI** additions to standard M7.

For this reason, the parametrization of Kerminen and Kulmala (2002) was applied to estimate the surviving fraction from diameter where nucleation is assumed to happen (1 nm in **PI** and 1.7 nm in **PV**) to 3 nm:

$$J_3 = J_n \exp\left[\left(\frac{1}{3\text{nm}} - \frac{1}{d_{pn}}\right)\frac{CS'}{GR}\gamma\right] \quad (2.2)$$

where J_3 is the NPF rate at 3 nm diameter, J_n is the nucleation rate ($\text{cm}^{-3}\text{s}^{-1}$), d_{pn} is the diameter of nucleated particles (nm), CS' is the reduced condensation sink (s^{-1}), GR is the growth rate (nm h^{-1}) and γ is a proportionality factor. The growth rate calculation included sulphuric acid concentrations and in **PV** also part of available gas phase organic vapours. As this process happens during one time step in the model (i.e. newly formed particles are directly put to 3 nm diameter), this parametrization will under predict the time needed to grow the particles to 3 nm size.

In the standard ECHAM5-HAM, all organic aerosol was represented in the model as primary organic aerosol (POM) with fixed mass ratio between the modes (Stier *et al.*, 2005). This is in contrast to studies suggesting that large fraction of organic matter in the aerosol particles are originally emitted in gas phase and, after oxidation(s), condensed to existing particles as secondary organic aerosol (SOA) (Tsigaridis and Kanakidou, 2003; Lack *et al.*, 2004; Fuzzi *et al.*, 2006). Addition of SOA was tested in **PI** using different oxidation yields of biogenic monoterpene emissions, mixing them in the boundary layer,

and condensing the resulting SOA to existing particles dynamically during the same model time step. This approach assumes that all of the oxidized monoterpenes will be completely non-volatile, but has the benefits of both including the organic aerosol derived growth in small particles and being computationally very cheap. In literature, many other approaches are used, with some using thermodynamical equilibrium models for organic condensation (O'Donnell *et al.*, 2011) and some are based on modelling the saturation vapour pressures over a wide range of values (Donahue *et al.*, 2012; Tost and Pringle, 2012). The approach used in **PI** and **PV** is simple, but it produces reasonable growth rates for submicron particles – a necessity to get realistic NPF rates.

The aerosol-cloud interactions in **PI** and **PV** are handled by activating the aerosol particles when the ECHAM5 expects clouds to be formed. The model uses the semi-empirical activation parameterization of Lin and Leaitch (1997). The method uses model-derived updraft velocities as an input parameter, and only uses the total aerosol number concentration above 70 nm in diameter as the representation of CCN. The actual cloud processes, including cloud droplet derived albedo changes, droplet autoconversion and precipitation are handled by the two-moment cloud scheme of Lohmann *et al.* (2007).

2.3 Implications of the **PI**

PI showed that the aerosol number concentrations are very sensitive to inclusion of nucleation. Even though the activation nucleation is not necessarily the best choice in many conditions (over oceans, upper atmosphere), it does, however, bring the aerosol number concentrations closer to the observed values in continental conditions. This conclusion is consistent with studies in the literature, done with other models and other nucleation parametrizations (Spracklen *et al.*, 2006; Merikanto *et al.*, 2009; Fountoukis *et al.*, 2012). However, the role of insufficiently characterized primary aerosol number emissions remain a problem to determine the actual level of NPF to the CCN concentrations (Spracklen *et al.*, 2010; Fountoukis *et al.*, 2012). The sensitivity of CCN concentrations to NPF makes the climate system sensitive to changes in available sulphuric acid. As a major source of H_2SO_4 is anthropogenic SO_2, changes in anthropogenic emissions could then significantly change the aerosol climate forcing. This result was one of the motivations to start work on the **PV**.

One of the key results was also the *ad-hoc* nature of the model/measurement comparisons. Even though some comparison data were available (CREATE database), there was little information or understanding what should be compared between the models and measurements. This issue was a the motivation for the work on **PII** and **PIII**.

3. EXPLORATION OF EUROPEAN AEROSOL

The sub-micron aerosol number concentrations have been measured since the 1890s, and number size distributions have been measured since the 1970s. However, different instruments, measurement standards and ways of representing the data can cause large differences in the measured distributions and concentrations, making generalization of aerosol properties from different measurements difficult. Another issue is to determine which properties of such distributions are important for different applications.

3.1 Measuring sub-micron atmospheric aerosols

The majority of submicron aerosol particles are well below the wavelengths of visible light (Fig. 2a). Thus direct optical measurement of particle concentrations is not feasible. Similarly, the mass of the submicron particles is very small, and especially the smallest nucleation mode particles have completely insignificant mass in comparison to particles in diameters closer to 1 μm (Fig. 2b). Direct measurements based on either of these properties will not be very useful to describe the submicron aerosol.

The first quantitative measurements of submicron (or to that matter, any) atmospheric aerosol particles were done in 1880s by J. Aitken, FRS, (Aitken, 1889b), measuring the aerosol **number concentrations** (N)[1] by growing the nanopartiles to larger sizes by condensation and counting them visually (Aitken, 1889a). Later improvements in the technology in the early 20^{th} century made possible to do continuous measurements of aerosol number concentrations (Mohnen and Hidy, 2010), leading to Condensation Particle Counter (CPC) instrumentation in the later half of the century (McMurry, 2000). The CPC instruments have their limitations. Depending on instrument architecture and operating fluid (commonly water or buthanol), they have different minimum measurable particle sizes, also subject to the particle composition. The major obvious limitation is that CPC measures only the aerosol total number concentration above some diameter – a bulk measure of the aerosol population. No knowledge of particle number size distribution is directly gained, but in many cases, no other long-term data of submicron aerosol concentrations are available (see **PIV**).

In **PII**, **PIII** and **PIV**, the instruments for aerosol particle number size distribution data were Differential Mobility Particle Sizer (DMPS) and Scanning Mobility Particle Sizer (SMPS). They are basically the

[1] Older texts prefer to use term Condensation Nuclei (CN) as the term for number concentrations measured with a CPC. This term is slightly misleading, as the original intent was to claim that **all** particles were counted in a CPC. Later studies showed that this was not the case in realistic CPCs (Liu and Kim, 1977). Even though CN terminology is still seen in some papers, it has clearly fallen out of fashion since 1980s.

same instrument, just driven with different instrument program. Both use a dried aerosol sample, get it to charge equilibrium using ionizing radiation, use the particle mobility in an electrical field to separate different sized particles and finally count them with a CPC. The DMPS changes the electric field voltage in steps to measure each size section sequentially, while the SMPS scans the measured size range with constantly varying voltage. Both instruments require periodic checks to run reliably. The differences between individual instrument measurements are minor between 20 and 200 nm (Wiedensohler *et al.*, 2012).

3.2 Collecting data and comparison parameters

One persistent problem in using datasets, even from organized database such as EBAS (http://ebas.nilu.no), is the quality control of time series. In most cases, the network responsible of the measurements have standardized the file format, meta-data information and the necessary data checks before submitting. However, analyses of the data revealed considerable variation in following these guidelines. Before using any of the time series in this thesis, I personally went through all of the datasets and consulted the data providers carefully for each probable rupture in the datasets. After correcting the obvious ruptures, the improved datasets were then re-uploaded to the database for the next user.

Just collecting the data together does not yet give great insights to the overall nature of atmospheric aerosol. One must do consistent choices how to start to reduce the data to more usable set. In **PII** I started to look the problem from modelling point of view, especially considering the aerosol indirect effects. As mentioned before, the number concentration of CCN is crucial for the aerosol indirect effects, and thus it was obvious that parameters related to CCN should be included in the comparison. For this reason, three proxies for CCNs from size distribution datasets were calculated, one as the total particle number from 50 to 500 nm (N_{50}), one from 100 to 500 nm (N_{100}) and one for 250 to 500 nm (N_{250}).

The next phase was then to select usable comparison metrics for the model/measurement comparison. Commonly the comparison between measured and modelled datasets have been done using arithmetic averages (e.g. some of the comparisons in **PI**). However, it is apparent that most aerosol properties are not normally distributed. The long tail towards high concentrations lead to a high sensitivity to the relatively rare outliers, making the comparison of arithmetic means between smooth modelled aerosol concentrations and noisy measurement time series difficult. In **PII**, the results suggested that the aerosol number concentrations are generally more closely log-normally distributed. Even this distribution is not always a good representation, as the overall shape is sometimes skewed, and thus the geometric mean is not always a good choice of comparison parameter either. In the end, most of the results in **PII** are given in percentile values, which do not assume any specific shape of the concentration distribution. This has the additional advantage of giving useful hints of the distribution shape and making the model/measurement comparison more complete.

The scale differences between model results and measurements also required some consideration. Especially when comparing a GCM in free circulation mode with measurements, the model can not be expected to produce directly comparable time series with the observations. Even GCMs nudged to meteorological re-analysis datasets can have difficulties in producing an exactly

comparable advection to measurements in shorter time scales. For these reasons, I chose seasonal distributions as the concentration comparison parameters. For special applications, the calculated number concentration time-series are also available in the comparison database.

3.3 European aerosol distributions

PII gives a quite comprehensive description of findings of the European size distribution datasets. However, it might be useful to compare the overall picture of number concentration data with mass concentrations. Figure 8 shows a simple comparison of annual median N_{100} from **PII** with (arithmentic mean) $PM_{2.5}$ concentrations from EMEP. The overall agreement between the levels of concentrations is relatively good, with clearest differences in Eastern Mediterranean, where $PM_{2.5}$ contains relatively large amount of dust, probably mostly absent from N_{100}. Another possible discrepancy was in the Po valley in Italy. Overall, this agreement just confirms the long-term similarities between aerosol properties, also shown by van Dingenen *et al.* (2004).

A surprising side result from the **PII** was the lack of weekly variation in the concentrations. Although the test done was somewhat questionable (see section 3.4.1), it raised some questions considering the current interpretation of aerosol weekday cycles in the literature.

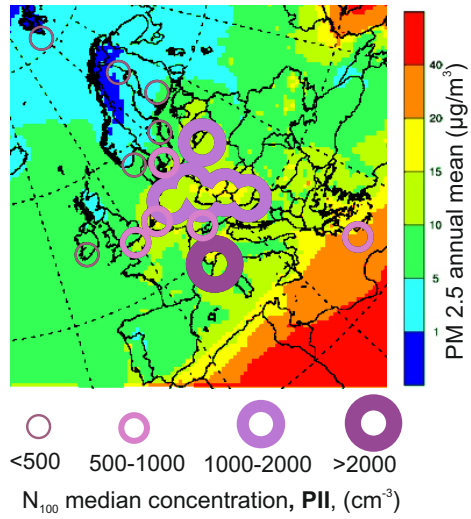

Fig. 8: Comparison of low-land N_{100} concentrations from **PII** with 2009 annual mean $PM_{2.5}$ concentrations based on EMAP/MSC-W model calculations and EMEP observation data, adapted from EMEP (2011) with permission.

3.4 The weekend effect

The *weekend effect* is based on observations of some meteorological parameters having an apparent difference between different weekdays. The name comes from most common assumption that the difference is between the working days and the weekend. Some studies use the more general term *weekday effect* for any such difference between the weekdays. One possible explanation for such differences would be the differences in anthropogenic emissions of primary aerosols or aerosol precursors in different days of the week. The importance of a weekday variation in meteorological parameters is apparent, as these anthropogenic source variation would then need to be taken into account in weather prediction. It would also be a strong evidence of aerosol-weather interactions, give indication of the strength of anthropogenic

influence on clouds, and could make the 7-day variability in the atmosphere a useful tracer of anthropogenic influence.

Some studies found clear differences between different weekdays temperatures or precipitation, others found none. Many of these differences can be attributed to technical errors (Daniel *et al.*, 2012), but the discussion the existence, spatial and temporal range, and reasons of the weekend effect still continues in the literature, of which Sanchez-Lorenzo *et al.* (2012) gives a recent review.

There is one thing that almost all of the studies however agree on: there is a weekend/weekday difference in aerosol concentrations. However, the concentrations used are either aerosol optical properties (in the form of aerosol optical depths) or, more commonly, aerosol mass concentrations from air quality networks. The aerosol mass concentrations are not necessarily a very good proxy for CCN concentrations, which are the key parameter in many aerosol indirect effects. On the few cases, where aerosol number concentrations or size distributions were used, the measurements are done very close to the emission regions in cities. Thus, a more directly cloud-related study of the aerosol variability in these time scales was needed, using the regional background data from **PII** and other sources.

3.4.1 Statistical properties of aerosol time series

The aerosol number concentrations are not necessarily well behaving time series in statistical sense. They exhibit strong autocorrelation in time scales used in many analyses and distributions of concentrations can be very far from normal distribution (see **PII**). Many commonly used statistical tests, such as t-test, explicitly assume normal distribution and independent measurements. The problematic features are general problems in many of the geophysical datasets, and methods have been developed to take these additional complexities into account.

In both **PII** and in **PIII**, the possible problem of non-Gaussian distributions was avoided by using a non-parametric test (U-test, or the related generalization Kruskall and Wallis test). The papers also take the specific features of aerosol number concentration time series into account by reducing the high hourly autocorrelation using only daily mean values, i.e. each data point in an analysed weekday time series has one week time difference from the next data point. When I wrote the papers, I thought that reducing the autocorrelation within each weekdays' concentrations is enough for statistical testing. After all, this is the methodology used in majority of studies in this field (e.g. Barmet *et al.*, 2009).

A recent publication by Daniel *et al.* (2012), showed that all autocorrelation effects are **not** removed by just daily averaging. Indeed, the statistical tests done in **PIII** are too conservative for the p value indicated, and are probably closer to tests done with $p < 0.01$[2]. Using the block bootstrap methodology described by Wilks (1997), a more realistic approximation of the statistical test significance could be made. Using their methods, 39 of 360 tests in **PIII** are statistically significant with $p<0.05$. If considering only seasonal tests (which are independent with each other), the results show 28 tests out

[2] In hindsight, this is is quite clear result. As the concentrations in the adjoining days are autocorrelated, a large part of their actual difference is masked by the persistence, leading to underestimation of the significance of concentration change. This is just an example how important it is to be very careful with statistical tests when there is significant autocorrelation in the datasets. Usually, some sort of bootstrap test is required, such as the one in the GLS/ARB trend analysis of **PIV**.

of 288 showing significant weekly variation. This is larger fraction of stations than would be expected by the p value chosen, and shows that there is some indication on weekday variation in European number concentrations. However, only one station showed consistent weekday variety. Otherwise the statistically significant weekday variations were not any way concentrated on specific size ranges, regions, or seasons. For the long term datasets, the Melpitz (MPZ) datasets showed statistically significant ($p<0.05$) weekly cycle for the whole year and autumn datasets for N_{50} and spring datasets for N_{100} and N_{250}. It should be mentioned that previous studies done with the exactly same, too conservative, test showed clear and strong weekday variability in PM concentrations – the overall weekday signal in CCN is thus much weaker than for PM.

3.4.2 Wavelet analysis

Dividing the time series to different weekday means and trying to extract statistically significant differences is a rather limited approach. The time window selection for such analyses is a natural limitation, and the high seasonal and other long-wavelength variabilities could mask short term weekday differences. Spectral methods are one way to try to extract specific period variations from the time series, and are considered specifically a powerful tool to study weekday variation (Bell and Rosenfeld, 2008).

Wavelet analysis is one method to separate the time series into a localized time-frequency spectra (Kumar and Foufoula-Georgiou, 1997). The time series is decomposed using a set of wavelets, with sensitivity to oscillations with different wavelengths. The continuous wavelet transform of discrete time series $x(t)$ of length N, with sampling time of δt is defined as

$$W(t,s) = \sum_{t'=t_0}^{N-1} x(t')\Psi(\eta(t',t,s))dt' \quad (3.1)$$

where W is the wavelet transform, $x(t)$ is the timeseries value at time t and Ψ is the normalized wavelet function (Torrence and Compo, 1998). In **PIII**, the Morlet(6) wavelet was used,

$$\Psi(\eta) = \left(\frac{\delta t}{s}\right)^{1/2} \pi^{1/4} e^{6i\eta - \eta^2/2}, \quad (3.2)$$

where η is the normalized "time" parameter

$$\eta = \frac{(t'-t)}{s}, \quad (3.3)$$

and s is the time scale parameter (s). Figure 9 gives an example of application of the continuous wavelet transform. The choice of Morlet(6) wavelet is common one and it is one of the most used wavelets in data analysis, where orthogonality is not usually needed, and it gives a good compromise between frequency and time space resolution (Torrence and Compo, 1998). The complex nature of Morlet wavelets makes possible to also get the wavelet transform phase $\varphi(t,s)$, which is the modus(2π) of the actual phase difference between the time series and the wavelet. The wavelet power spectrum $P(t,s)$ is given by

$$P(t,s) = |W(t,s)|^2. \quad (3.4)$$

In wavelet analysis, the wavelets are then scaled in frequencies by adjusting the scale parameter s, and repeating the transform for all the needed wavelengths (Figure 9d). The actual choice of scales in this kind of analysis is arbitrary, but scales below two times sampling period or larger than approximately half of the time series length give no further information.

The wavelet transform also contains the noise in the original signal. Statistical

tests thus are also needed in wavelet analysis to distinguish probable signals from noisy background. The statistical test part of **PIII** wavelet analysis is based on the approach by Torrence and Compo (1998), which compares the observed wavelet powers to similar powers from first order autoregressive (AR(1)) noise:

$$x(t + \delta t) = \alpha x(t) + e, \qquad (3.5)$$

where $x(t)$ is the noise timeseries, α is the autocorrelation coefficient and e is random Gaussian white noise. An estimate of the wavelet AR(1) power spectrum comes from discrete Fourier spectrum of AR(1) noise (Gilman *et al.*, 1963)

$$P_n = \frac{1 - \alpha^2}{1 + \alpha^2 - 2\alpha \cos(2\pi \delta t / \lambda_f)}. \qquad (3.6)$$

The confidence intervals of such noise spectrum are then created using the inverse χ^2_2 distribution, which requires somewhat normal distribution of the original data. The used α values were from datasets which were de-seasoned by subtracting a 90 day moving average. However, the trend was not removed from these signals, and the autocorrelation might have then been overestimated, leading to overestimation the signal-to-noise ratio in **PIII**. The analysis used thus should show slightly too significant signals. Note that the overall applicability of the analysis depends that the estimated signal *can* be modelled with a stationary AR(1) noise. As no clear band of signal was detected in the wavelet power spectra (Figure S1 in the supplementary material of **PIII**), I am confident that the 7-day signal was generally absent in the data series analysed.

3.4.3 Lack of weekly waves or not?

The conclusions in **PIII** are somewhat changed due the inconsistencies in the statistical analysis. There are some signs of CCN driven weekend effect in some parts of European background. The statistically significant variations in some Central European stations are consistent with earlier findings, but much weaker and rarer than generally accepted in the literature. The very same (too conservative) tests in earlier work by Barmet *et al.* (2009) did show highly significant trends in PM, which is a clear indication that the weekly trends in CCN sized aerosol particles have much less clear weekly signal than in aerosol mass parameters. Thus the discussion part of **PIII** is still valid.

The lack of variation in wavelet analysis requires then some more discussion, due to inconsistency with statistical tests in the MPZ dataset. I re-analyzed the long datasets of MPZ with wavelet analysis, but I could not detect a clear 7-day oscillation in the spectra. However, what is clearly seen even in Figure 4F of **PIII**, is an oscillation with 14 day wavelength. This could then mean that, at least in MPZ, the oscillations could be more commonly bi-weekly than weekly in nature.

Overall, the weekday signal is not so clearly seen in the CCN concentrations as it has been seen for the particle mass. The variability of particles dominating the CCN numbers in weekly time scales is very different from the variability of larger (or smaller) particles. Thus, using either optical, or mass based proxies for CCN is very error prone in these timescales. Generalizing aerosol variation from property (or diameter range) to another should always be done with some consideration.

Another issue altogether is the implicit assumption that only anthropogenic processes can create 7-day cycles. Kim *et al.* (2010) suggested that some natural atmospheric processes could also create such oscillations, previously also hypothesised by Forster and Solomon (2003). Thus differen-

tiating between natural and anthropogenic influences might not be as straightforward as previously thought. This was the reason why **PIII** had the phase analysis for the results of the 7-day variation.

The aerosol mass concentrations do show weekly variability in the literature, and recent studies have shown that the effect of so-called giant CCN (in the particle diameters above 1 μm) can have a strong effect on the rain formation in some clouds (Konwar *et al.*, 2012). This could be an avenue how the weekend-effect works, outside of the measurement range of datasets used in **PIII**. It might also be that due to the effects of these giant CCN, the earlier studies using $PM_{2.5}$ could have co-incidentally used a usable proxy for the actually effective aerosol property for weekend effect, just not the property they were after.

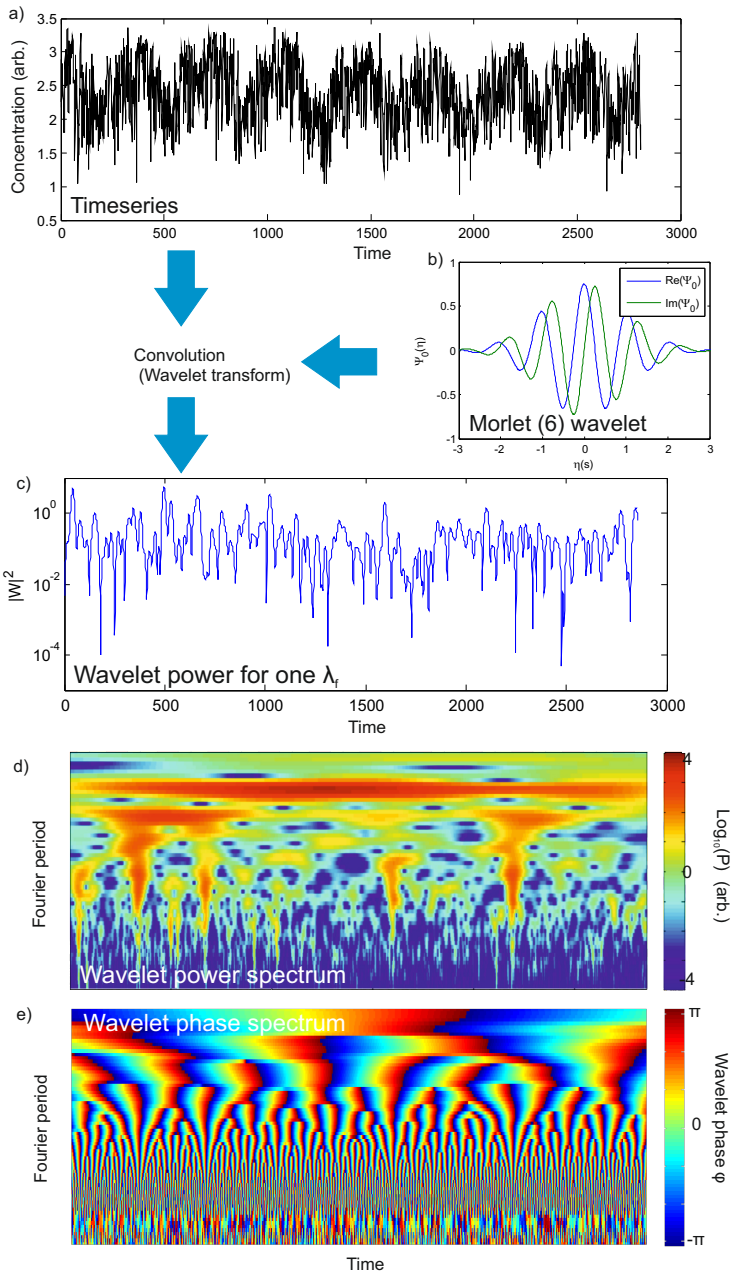

Fig. 9: Schematic example of the wavelet analysis. The timeseries (a) is transformed in a continuous wavelet transform (eq. 3.1) with the Morlet(6) wavelet. Resulting wavelet power for one scale (or Fourier wavelength λ_f) is shown in (c), showing how strong the signal of this wavelength was in the sample in the neighborough of each measurement time. Repeating the wavelet transform over a range of wavelengths, a power spectrum (d) and a phase spectrum (e) can be obtained as a function of time. No considerations of data gaps or edge effects are presented.

4. "STUDY THE PAST IF YOU WOULD DEFINE THE FUTURE"

PI suggested that the aerosol number concentrations and CCN number concentrations are very sensitive to new particle formation. The majority of new particle formation parametrizations and laboratory experiments are strongly controlled by the amount of sulphur in the system, suggesting a large role of the sulphur also in the atmospheric new particle formation. Thus the changes in available sulphur in the atmosphere should affect the aerosol concentrations and the aerosol-climate interactions. The emissions of sulphur dioxide were (and, in some cases still are) the main reason for the acid rain, and thus from the 1980s and on, the emissions of SO_2 have been radically cut in North America and in Europe. The title of this chapter is a quote from Confusius (551-479 BCE), well characterizing the methodology which is used here: Is the decrease in SO_2 emissions evident in the past aerosol number concentrations? Are the future aerosol properties strongly influenced by the further changes in anthropogenic emissions?

4.1 Trends of the past

The IPCC AR5 Working Group I asked the Global Atmosphere Watch to produce a study on aerosol in-situ measurements trends. After some discussion, it was decided that me and Dr. Martine Collaud Coen would do this study, splitting the task into two: I analysed the aerosol number concentrations and number size distribution datasets (**PIV**), and Dr. Collaud Coen analysed the in-situ optical property datasets (Collaud Coen *et al.*, 2012). The main motivation for these studies was to find out if any trends are visible in the long term datasets, provide trend information for decadal scale modelling efforts, and to give some indication of probable trend drivers.

The methodologies which I adapted for these studies (GLS/ARB and GLS/MBB) are explained in detail in **PIV**. Figure 10 shows in a more graphical way the basic idea behind the AR bootstrapping process used.

As it is not directly explained in **PIV**, it might be useful to explain shortly also the other method (Sen's slope connected to Mann-Kendall test) used in the trend fitting. The Sen's slope estimator for the trends is a non-parametric approach, where each possible pair of the measurements

$$[x(t(i)), x(t(j))] \ , j > i \qquad (4.1)$$

was fitted a slope, and the median of these slopes was used as the trend estimator (Sen, 1968). In practice, this was done for daily or two daily median values, depending on data size. The significance of these trends were then estimated using a seasonal Mann-Kendall (MK) test, which is a non-parametric technique based on rank (Hirsch *et al.*, 1982). In the Mann-Kendall trend test, the correlation between the rank order of the observed values and their order in time is considered. The most obvious

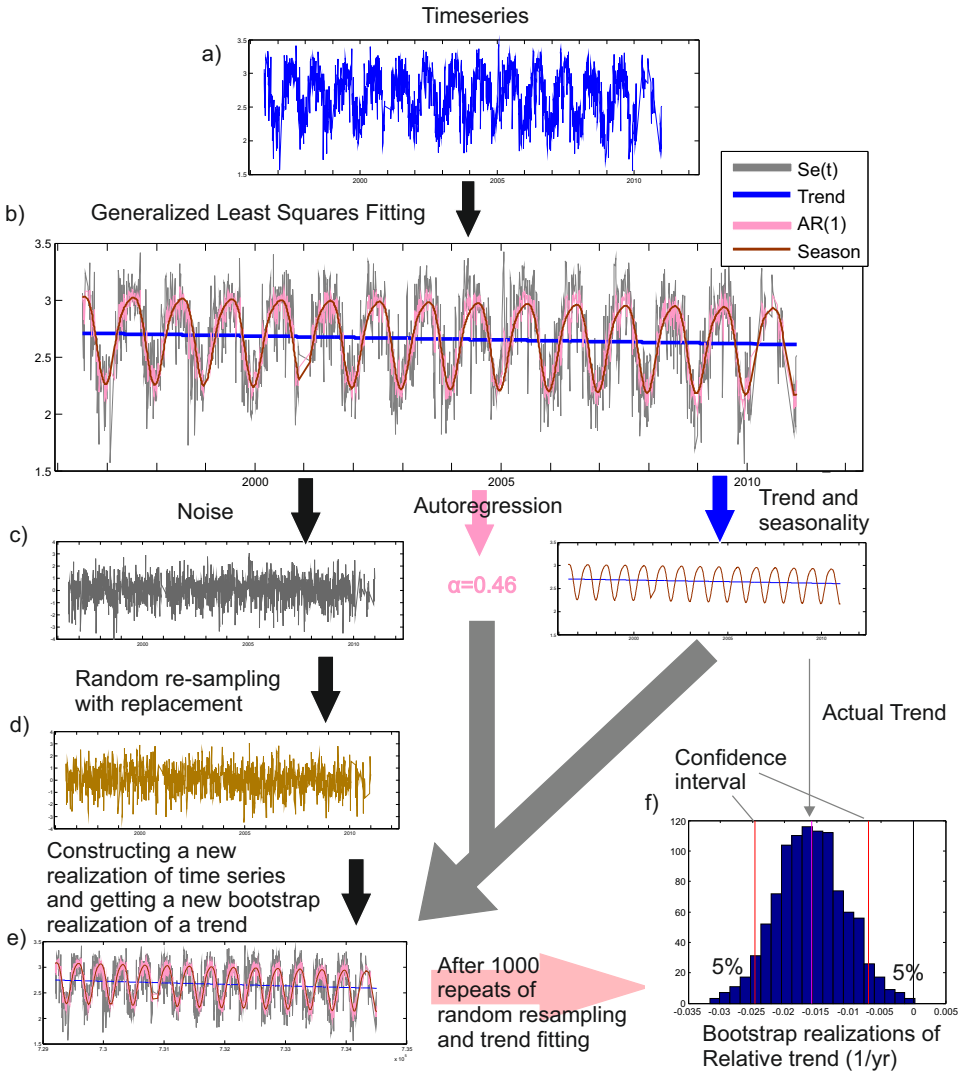

Fig. 10: More graphical version of the upper part of Figure 1 in **PIV**explaining the ARB method of trend confidence interval generation. a) Timeseries analyzed (Pallas, Finland), b)-c) GLS is used to separate the dataset to trend, season, autoregressive part (AR(1)) and noise ($Se(t)$). d) Noise terms are re-sampled and using AR(1), trend and season of the original GLS fit, e) a new trend is fitted and saved. After 1000 repeats of d)-e) a bootrapped distribution of trend slopes is obtained and confidence interval can be generated from 5th and 95th percentile points.

advantage of the MK test is that the data do not need to conform to any particular distribution. However, as the MK test is sensitive to autocorrelation in the dataset, the data had to be first pre-whitened using the method described by Wang and Swail (2001): (1) estimate the auto-correlation, (2) if the auto-correlation is higher than 0.05, calculate the Sens slope, (3) remove the linear trend using the Sens slope, (4) remove the auto-correlation (whitening), until $\alpha < 0.05$ and (5) add the trend. The pre-whitening routine is always a compromise between too strong removal (where part of the actual signal is lost) and too little (where some of the AR noise is left in the dataset, possibly affecting the trend fitting). The test for either an upward or downward trend was the two-tailed MK test at the 95% level of significance.

The trends in **PIV** show signs of decreases in the number concentrations in many locations. The lack of data does not yet allow us to conclude that this change has been global. The analysis of trend drivers in **PIV** is basic, but in my opinion sufficient for a paper this concentrated on the data analysis. The potential role of SO_2 can, however, direct future research. A comprehensive comparison with potential trend drivers should be done using GCM simulations, more advanced methods capable of taking into account several potential explanatory processes into at the same time, as well as capable in some extent to evaluate the importance of different feedbacks in the system. The results of the trend analysis papers were recently presented in a AEROCOM modelling workshop, and there is a good chance that such studies will be done shortly.

The climate system is full of feedbacks related to aerosol particles: air temperature is affected by the aerosol concentrations via aerosol-climate interactions; increase in temperature could affect the emissions of dimethyl sulphide, creating more particles and acting as a cooling effect (so called CLAW hypothesis; Charlson *et al.* (1987)); cooling feedbacks could be detected from an increase in terrestrial plant VOC emissions (Kulmala *et al.*, 2004c; Arneth *et al.*, 2009); changes in wind speeds could affect fluxes of sea salt and DMS (Carslaw *et al.*, 2010); increased sea surface temperatures could reduce the emissions from sea spray (Mårtensson *et al.*, 2003; Zábori *et al.*, 2012a,b); decreased sea ice could increase the marine sources of aerosols (Nilsson *et al.*, 2001; Struthers *et al.*, 2011); changes in precipitation could affect aerosol concentrations (Iversen *et al.*, 2010). Even considering such potential feedbacks, I find the rather strong similarity of SO_2 trends with the observed N trends, especially from the viewpoint of the good understanding of relationship between SO_2 and aerosol particle number concentrations, a good candidate of number concentration trends in the US and parts of EU.

4.2 A view to the future

PIV showed that number concentration trends have been decreasing, and there are some evidence that this could also have been happening to CCN concentrations. If the simplified analysis of **PIV** regarding the role of anthropogenic emissions is valid, this raises some concern on future emission cuts.

The future anthropogenic emissions trends are of much dependent on the policies we adopt in the next decades. As there are a wide variety of potential choices, IPCC formed specific task force to generate Representational Concentration Pathways (RCPs). These pathways give the latest IPCC AR5 simulations a comparable set of alternative future concentrations. Unlike the earlier SRES predictions (Nakicenovic *et al.*, 2000), the RCPs did not start di-

rectly as emission scenarios, but instead are internally consistent sets of projections of the components of radiative forcing that are used in subsequent phases of IPCC modelling work with concentrations as the primary product. In total, a set of four harmonized pathways were produced that lead to radiative forcing levels of 8.5, 6, 4.5 and 2.6 Wm^{-2} by the end of the century (van Vuuren *et al.*, 2011). Of these, the **PV** used all except RCP6, which was not yet completely characterized when the simulations were done.

Figure 11 shows a collection of current estimates of past and future anthropogenic SO_2 emissions. The future emission estimates show a high variability in SRES emission inventories (grey area), the extreme scenarios of Cofala *et al.* (2007), and the current IPCC AR5 derived Representational Concentration Pathway (RCP) emission pathways. Notably, all RCPs lead to almost pre-industrial anthropogenic SO_2 emissions by 2100.

The key issue with RCPs was that they only considered the concentration pathways of anthropogenic emissions, and thus the level of biogenic or other natural emissions are left to be estimated by the climate models. As the simulations in **PV** were relatively short (5 years) snapshots of effects of different period emissions, the long-period changes in e.g. ocean circulation or vegetation changes were not taken into account.

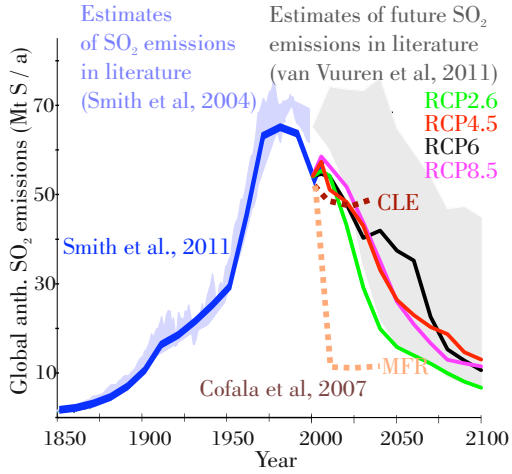

Fig. 11: Evolution of anthropogenic SO_2 emissions. CLE and MFR correspond to "current legistlation" and "maximum feasible reductions" by Cofala *et al.* (2007), used in Kloster *et al.* (2008, 2010).

To simulate some of the possible long-term natural feedbacks, the **PV** included variation of both oceanic Dimethyl Sulphide (DMS) and biogenic VOC emissions on the scale presented in other literature. Another important thing to notice is that the **PV** simulations were done for the current day climate, i.e. by keeping the sea surface temperatures in current climate conditions and thus the overall global mean temperature was not allowed to drift strongly. This was necessary, as otherwise the separation of aerosol-induced changes to the radiative forcing could have been challenging to be distinguished from temperature driven changes in the atmosphere. Fixing the sea surface temperatures also suppresses temperature driven changes in the the sea salt emissions (e.g. Mårtensson *et al.*, 2003).

4.2.1 Radiative forcing

The sensitivity of the global climate to different changes in the driving factors is not trivial to determine. The most obvious

choice would be to run the model after each change as long as it is needed for the climatological temperature to reach a new stable regime. However, this stabilization takes quite a long time in the climate models, not to mention the additional complexity of including a coupled complete ocean-atmosphere model to take the ocean heat capacity and mixing into account. Typical time scales for such changes are of the order of tens of years (Hansen *et al.*, 1981; Brasseur and Roeckner, 2005; Kloster *et al.*, 2010), which are, considering the overall time scales of aerosol processes and atmospheric variability, quite expensive computationally.

There are, however, other methods to estimate the effects of aerosol concentration perturbations on the climate system. For the direct aerosol effects, a change in the model estimate of Aerosol Optical Depth (AOD) is sufficient to approximate the effects. For indirect effects, no such direct parameter is available, and the climate system response is approached from the concept of radiative forcing (RF), specifically radiative flux perturbation derived radiative forcing.

In short, the radiative forcing is a term describing the immediate change in the atmospheric radiative balance from a perturbation, and can be connected to temperature by use of climate sensitivities. IPCC definition of RF is "the change of net (down minus up) irradiance (solar plus longwave; in Wm^{-2}) at the tropopause after allowing for stratospheric temperatures to re-adjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values" (Ramaswamy *et al.*, 2001). This definition of RF has been useful in comparing the immediate relative radiative effect of different consistuents of climate change (typically compared to pre-industrial levels), but it has severe limitations for aerosol-cloud interactions, where the relatively fast, but not instantaneous, changes in e.g. cloud lifetime could have a strong effect (Lohmann *et al.*, 2010). For this reason, the radiative forcings in the **PV** were calculated directly from radiative flux perturbations (RFPs) (i.e. changes in the mean incoming and out-coming radiation fluxes) in the simulations while keeping the sea surface temperatures at current climate values. This results in values comparable with traditional RF, but still allowing for finite time response of the aerosol-cloud interactions to play a role (Lohmann *et al.*, 2010).

5. REPERCUSSIONS AND PERSPECTIVES

The tasks of the Finnish universities (research, teaching, etc.) are supposed to be done with the viewpoint of promoting societal impacts (Yliopistolaki "University law" 2§). From this standpoint, it is necessary to not only consider scientific conclusions, but also to think what are the possibly wider consequences of results of this thesis.

Small particles are not good for your health (Section 1.4.2), and some actions towards lowering the particle number concentrations have already been implemented. As an example, recent European Commission directives for vehicle emissions include a limit to particle number emission rates for particles larger than 23 nm in diameter (EC, 2008). If these efforts limiting the aerosol particle number concentrations lead to air quality directives, one of the first things to evaluate would be the current background concentrations. The **PII** results give the first consistent analysis of the outside-of-cities concentrations and variability in Europe.

The results in **PII** and to lesser extent other papers of this thesis show the high importance of biogenic processes to these concentrations. This complex interaction between anthropogenic and biogenic emissions might lead to serious difficulties determining the most cost-effective strategies for number concentration reductions. The relatively long lifetimes of large fraction of aerosol number concentration, as evidenced in **PIII**, lead to obvious difficulties determining the source areas of any increased concentrations. Overall, the reduction strategies would probably get very challenging to formulate for particulate number concentrations.

The **PII** also provided a dataset and methodologies to do comprehensive comparisons between the models and measurements. This dataset has already shown to be practical in some modelling studies (Knote *et al.*, 2011; Reddington *et al.*, 2011; Bergman *et al.*, 2012; Mann *et al.*, 2012; Fountoukis *et al.*, 2012), and at least a few other groups have already contacted me on the details of using the dataset. Overall, this work in **PII** seem to have been useful for the community.

The existence or non-existence of the weekend (or weekday) effect might not be so clear indicator of aerosol-cloud interactions as previously considered. The results of **PIII** show that the CCN concentrations are much less sensitive to the weekday variation in the emissions of aerosol particles or particle precursors. The main reasons for this lack of periodicity are different measurement locations, processes affecting concentrations and especially, different lifetimes of CCN sized particles in comparison to $PM_{2.5}$ or PM_{10}. The lack of weekday periodicity in CCN will also suggest that if there is no weekly variation in the meteorological properties, it is not necessarily an indication of a weakness of aerosol-cloud interactions.

Long-term time series of N show generally decreasing trends (**PIV**). No clear sin-

gle reason for the decreasing trends could be found, but the overall trend of SO_2 emissions do show some promise as an explanatory driver in Northern Europe and America. This shows that reduction in aerosol precursors could, at least in polluted regions, reduce the number concentrations significantly. The lack of long-term data make conclusions on the changes in CCN still uncertain from measurement point of view. However, the results of **PV**, Kloster *et al.* (2008, 2010) and Fountoukis *et al.* (2012) strongly suggest significant sensitivity of CCN concentrations to emission changes. How important this CCN change for our current climate has been, and if the current models even can capture such trends in N or CCN, is not yet known. Comprehensive model results could also provide much better view on potential biogenic or oceanic aerosol feedbacks on the climate system and on their roles in aerosol trends.

The global number concentrations, as simulated by ECHAM-HAM simulations in **PI**, are sensitive to the inclusion of new particle formation. This inclusion also improves model performance, and changes the CCN concentrations significantly. As the new particle formation is dependent on sulphuric acid concentrations, the results suggest that the atmosphere could be more sensitive to the amount of sulphur emitted than would be expected without NPF. This sensitivity is highlighted in **PV**, where the current day aerosol forcing is increased significantly by inclusion of boundary layer new particle formation. The **PV** also suggested a strong warming effect of radical emission reductions prognosed by IPCC emission pathways, mainly from aerosol indirect effects on clouds.

The importance of SO_2 emissions changes to aerosol forcing is perhaps even better underlined by comparing the emission reductions to the proposed climate engineering methods. The atmospheric science community has been very hesitant to promote climate engineering methods, due to potential unforeseen consequences. Climate engineering methods have high inherent risks, could significantly make the situation worse in the long run, could force us to long-term upkeep of potentially hazardous operations, and could reduce the motivation to work with the actually important (but expensive) emission reductions of greenhouse gasses (Robock, 2008). Recent studies have shown that the climate cooling forcing of affordable climate engineering efforts are close to similar magnitude as the warming forcing from emission reductions in **PV** (Shepherd *et al.*, 2009). In the climate engineering, a positive effect (cooling) is expected, but we are not sure of the adverse side effects. In the case of the aerosol emission decreases, a negative climatic effect (warming) is suggested in **PV** and other studies (Brasseur and Roeckner, 2005; Andreae *et al.*, 2005; Kloster *et al.*, 2008, 2010), although such changes will have positive effects on air quality (Löndahl *et al.*, 2010).

In this context, it is unfortunate if the society (including the atmospheric research community) is not considering the climate effects (including aerosol indirect effects) in impact assessment of the emission reductions. Such considerations are necessary especially considering adverse effects of extreme weather on population health (McMichael *et al.*, 2006). As an example, the impact assessment summary of the recent directive to reduce sulphur content in marine fuels does not have any mention on negative impacts to climate (EC, 2011), instead concentrating on economical and health impacts. The health impact assessments are done only for changes in total particulate mass (PM), although the increase of SO_4 might not always lead to increased adverse long term health effects (Heyder *et al.*, 2009). The latest European Environment Agency report does, however,

already acknowledge the potential of adverse side effects to climate from air quality directives, with comment that current models are still incapable to describe particles in the atmosphere and the aerosol-cloud interactions (EEA, 2012). Perhaps in the future, also potential warming impacts will be assessed more in detail.

On the other hand, all studies of SO_2 reduction side-effects using detailed aerosol microphysics (including **PV**) are done with versions the same GCM: ECHAM5-HAM (Kloster *et al.*, 2008, 2010). I was recently informed that there is a possibly an overestimation of the SO_2 levels in ECHAM5-HAM, leading to possible too high sensitivity on sulphur emissions (Dr. Declan O'Donnell, personal communication, 2012). This effect is still unknown, but could result in smaller overall aerosol climate effect in the model calculations, and thus smaller overall current day-to-future differences. However, the studies done with models without detailed aerosol microphysics still give high warming potential to anthropogenic aerosol emissions cuts (e.g. Brasseur and Roeckner, 2005; Andreae *et al.*, 2005; Lamarque *et al.*, 2011), and thus the effect of this possible overestimation of SO_2 is probably only a matter of scale.

One could think that we have already done a long time "accidental climate engineering"[1] by inclusion of sulphur dioxide and primary particle emissions in the atmosphere. Now removing this cooling effect will bring us closer to the pre-industrial situation in one aspect, but due to the increase in the CO_2 and other long-lived climate warming gases, in a completely different end result. The rapidness of aerosol removal in the atmosphere should be considered, and the reductions in aerosol emissions should be perhaps concentrated to locations where their impact on air quality is largest, and their relative climate impact is smallest. As the aerosol-cloud interaction saturates at high CCN concentrations, perhaps the best is to reduce the SO_2 emissions close to regions with already high aerosol loading, and consider even increasing the emissions in regions with low aerosol loads, such as over the oceans. Naturally, the potential ecosystem damages e.g. from increased acidity should be taken into account as well. These are just rough common sense estimates, and actual policy decisions should be done using best possible knowledge of the trade-offs required.

This discussion of SO_2 reductions should not be taken as a promotion for climate engineering, or as promoting sulphur emissions. I consider these possible adverse effects of emission reductions as a warning example of the kind of side effects climate engineering mechanisms can bring. The potential side effects of SO_2 reductions are comparable to the "termination effect" risk of the climate engineering mentioned by (Shepherd *et al.*, 2009) and could thus be an indicative of the kinds of quagmires we might end up if we actually start to use climate engineering methods in the future.

Research needs

Model-measurement comparisons of CCN sized particles are still not satisfactory, at least in the global scale. The lack of long time series of number concentration data in many parts of world limit the possibility to do comprehensive mode/data comparisons. The dearth of data is even worse for the number size distributions. Acquiring long-term data series require strong commitment, not only from measurement groups, but from the funding agencies as well. For this thesis, the work done in the

[1] "Accidental climate engineering" is slightly inaccurate terminology – most definitions require climate engineering to be intentional.

frameworks of GAW, EUSAAR and later ACTRIS were very valuable, and hopefully such networks continue to operate and even expand. The lack of long-term data in South America, Africa, Asia, Australasia and over the oceans is crippling for a good evaluation of the model performance. Perhaps even harder to achieve would be long-term data series from the marine boundary layer, and from the free troposphere. Shorter-time measurements can be a substitute for some applications, but for a robust comparison, statistical properties from long term datasets are the only really useful comparison parameters for GCMs.

There is almost no information on the ambient number size distributions of supermicron aerosol particles. There are only a few stations reporting reliable number concentration data from this size range, and thus the models' abilities to predict these concentrations, and related aerosol-cloud interactions, are still poorly constrained.

Using datasets from networks even with high standards in measurement quality can sometimes be challenging. The use of the data sometimes needs significant extra work from the data user, in the form of additional quality checking and communicating with the data provider. Even finding the correct datasets can be challenging, and the data formats, measurement standards and data usage policies can widely differ in different networks. There are currently several international projects working on making such environmental data easier to obtain[2].

Going through monitoring data requires a lot of expertise on what is expected from the data measurements. The data cleaning is also very time consuming and labour intensive. Hopefully, the current tendency towards providing datasets peer review[3], and citable persistent document identifiers (e.g. Digital Object Identifier, DOI)[4], will improve incentives and resources for data quality checking. When these data citations are also stored in scientific citation databases, the production of quality data can be better taken into account when evaluating personal achievements. The resources needed for the data processing and submission should also be explicitly reserved in the finance plans of measurement projects.

The model/measurement intercomparisons is further hampered by the limited spatial and temporal resolutions the GCMs can work with. The differences of local measurements and large spatial scale grid boxes of models can create many problems for the comparisons. In GCMs many processes are already highly parametrized due to their sub-grid nature, and such approaches could as well be used for the aerosol-climate interactions. Especially considering the high sensitivity of NPF to background aerosol and condensible vapour concentrations, the sub-grid variability in near emission source regions could be important and should be better characterised for the global models.

Another issue with model resolution is the availability of short-scale (diurnal or weekly) temporal variation in different emissions. In ECHAM5-HAM, most of the emissions of aerosols and precursors are emitted using monthly-mean 2D emission fields, i.e. no short-term temporal variability was considered. Again, considering the short time scales of many aerosol processes, this averaging approach can lead to very dif-

[2] I am currently involved in two such international projects, European ENVRI (http://envri.eu/) and Europe-US COOPEUS (http://www.coopeus.eu/)

[3] e.g. Earth System Science Data (ESSD) data journal, http://www.earth-system-science-data.net/

[4] e.g. PANGAEA project, http://www.pangaea.de/ stores environmental datasets, provides them with DOIs and provides search for different properties. I intend to supply the **PII** dataset to there within this year if the co-authors agree.

ferent results than has been seen in the nature.

Similarly, the emissions are usually poorly characterized in sub micron size ranges, often only PM emissions are prescripted, and constant PM-to-number size distribution factors are used globally (Textor *et al.*, 2007). The model results are necessarily very sensitive to these conversion factors (Spracklen *et al.*, 2010), and more consistent bottom-up approaches to emissions, such as recent European number size distribution emission inventory (Kulmala *et al.*, 2011), are needed. The modelling studies to study the importance of primary vs. secondary particle concentrations have already shown the benefits of these emission approaches in Europe (Reddington *et al.*, 2011).

There are still a lot of uncertainty from the feedbacks in the Earth system, which could easily affect the aerosol-climate interactions (Carslaw *et al.*, 2010). More information on biosphere-climate interactions (via e.g. temperature effects on VOC emissions); ocean-climate interactions (via e.g. sea-spray or DMS emissions); or even climate-dependent changes in anthropogenic emissions (e.g. changes in domestic combustion change in warming climate) are needed. Answers to these problems require a lot of new work, not only on process scale, but also on developing Earth System Models with the capabilities to handle these dynamics.

Another quite significant drawback in the current ECHAM5-HAM is the lack of on-line oxidant chemistry. For performance reasons, the ECHAM5-HAM uses prescribed monthly OH fields, although with solar radiation scaling. Such approaches are very crude, especially considering the influence of OH fields on SO_2 oxidation to sulphuric acid. The oxidant fields are even more important when considering more realistic approaches to gas and liquid phase organic or nitrate chemistry, especially on the generation of additional oxidants from the organic species themselves (Mauldin III *et al.*, 2012) or from nitrates in the soil (Su *et al.*, 2011).

The models themselves can always be improved process-wise. Studies in this thesis and otherwise have shown the importance of the new particle formation to the climate system. Mechanistic approaches to the nucleation mechanism should improve the simulations of especially past and future conditions, where the applicability of semi-empirical relationships – developed in current atmospheric chemistry background – might not be relevant. Notably, most of the NPF parameterisations are based on measurements in a limited range of different environments, making even generalisations in current climate suspect. Recent work on very advanced laboratory measurements in CERN (CLOUD project) are very promising in this respect (Kirkby *et al.*, 2011). Even though the physico-chemical processes of the atmospheric nucleation would be determined, we will also need realistic knowledge on the concentrations and properties of organic and inorganic vapours responsible for the particle growth.

The aerosol-cloud interactions in GCMs are necessarily very simplified. There are a few aspects of the current parametrizations that are known to represent the aerosol poorly: Currently ECHAM assumes a constant entrainment rate for the convective clouds. This parameter is actually one of the key tuning parameters of the model, and thus considered to be a relatively free parameter. An other assumption is the simplistic idea of adiabatic cloud systems. Almost all GCMs use the idea of adiabatically rising air parcels (with highly parameterised updraft velocities) as the basis of CCN activation and subsequent cloud-top CDNC. This approach does not specif-

ically take into account 3D complex nature of the clouds, and some studies have shown that droplets can participate several activation-evaporation cycles before ending up in the cloud-top (Flossmann and Wobrock, 2010). The development of a parametrization which includes such effects will be very challenging. Similarly, the onset of ice nucleation is a critical factor on rain formation; the level of knowledge in this field is still far from the level needed for comprehensive climate impact assessment (Curry and Khvorostyanov, 2012).

Overall, the GCMs will require a more complete and systematic evaluation of effects of uncertainty to the climate parameters. Such studies have been done for global chemistry transport models (Lee *et al.*, 2012) and for more traditional climate models without interactive aerosols (Knight *et al.*, 2007), and they could guide the research towards the more uncertain parts of the modelling systems.

Efforts should also be used towards using and developing more advanced methods of data mining and analysis. I chose the wavelet analysis used in **PIII** to find new information from older datasets. This approach could be further developed using e.g wavelet coherency analysis to determine in which time scales different time-series behave similarly. That and other such methods can prove to be critical to analyse possible long-term influences in the variability of climate relevant factors in the atmosphere. During the next decades, new and innovative approaches to data generation, data analysis, modelling and science management are needed.

SUMMARY OF PUBLICATIONS AND AUTHOR CONTRIBUTION

PI Makkonen, R., **Asmi, A.**, Korhonen, H., Kokkola, H., Järvenoja, S., Räisänen, P., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., Järvinen, H., Lohmann, U., Bennartz, R., Feichter, J., and Kulmala, M. (2009). Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5–HAM global circulation model. *Atmospheric Chemistry and Physics*, 9(5):1747–1766. $^{(a)}$

Overview: A modelling paper, where we used ECHAM5-HAM model to calculate the sensitivity of CDNC concentrations to different boundary layer nucleation schemes. The overall conclusions of this paper are that the boundary layer NPF can influence the climate in significant way, although the use of single value for activation coefficient can lead to overestimation of aerosol number concentrations. The addition of different approach to organic aerosol handling was also tested.

Author contribution: I planned together with R. Makkonen and V.-M. Kerminen the experiments, and we also did the interpretation of the results together. I wrote the initial discussion part of the paper (which ended up in the final version almost in verbatim), and wrote together with R. Makkonen the conclusions of the paper. I did also small part of the coding.

PII **Asmi, A.**, Wiedensohler, A., Laj, P., Fjaeraa, A.-M., Sellegri, K., Birmili, W., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P., Hansson, H.-C., Fiebig, M., Kivekäs, N., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P. P., Swietlicki, E., Kristensson, A., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G., Henzing, B., Harrison, R. M., Beddows, D., O'Dowd, C., Jennings, S. G., Flentje, H., Weinhold, K., Meinhardt, F., Ries, L., and Kulmala, M. (2011). Number size distributions and seasonality of submicron particles in Europe 2008-2009. *Atmospheric Chemistry and Physics*, 11(11):5505–5538. $^{(b)}$

Overview: A data analysis paper, which combined aerosol number size distribution measurements from 24 stations around Europe. This resulted in a set of metrics which has already been used in model evaluation. The dataset also provides harmonized and reliable way to establish the current variability of regional background aerosol size distributions in Europe.

Author contribution: I had the original idea of the paper (with some input from C. O'Dowd). I used ready-made datasets from the EBAS data repository (i.e. I did not do any measurements), programmed the analysis codes, wrote most of the article, decided on the chosen metrics, methods of analysis and made the figures and tables.

PIII **Asmi, A.** (2012). Weakness of the weekend effect in aerosol number concentrations. *Atmospheric Environment*, 11(11):5505–5538. [(c)]

Overview: A short data analysis paper, where I used spectral and statistical methods to show that there is no strong 7-day (i.e. potentially directly anthropogenic) oscillation in European regional background of CCNs or CCN-sized aerosol particle number concentrations. Reasons for this disparity are discussed, and I show that the aerosol in the smaller CCN-sizes contributing to convective cloud CDNC, are behaving much differently from the larger aerosol measured in PM monitors.

Author contribution: I was the only scientific contributor, the data was from the data providers, but all analyses were done by me.

PIV **Asmi, A.**, M. Collaud Coen, J. A. Ogren, E. Andrews, P. Sheridan, A. Jefferson, E. Weingartner, U. Baltensperger, N. Bukowiecki, H. Lihavainen, N. Kivekäs, E. Asmi, P. P. Aalto, M. Kulmala, A. Wiedensohler, W. Birmili, A. Hamed, C. ODowd, S.G. Jennings, R. Weller, H. Flentje, A. M. Fjaeraa, M. Fiebig, C. L. Myhre, A. G. Hallar, and P. Laj (2012). Aerosol decadal trends (II): In-situ aerosol particle number concentrations at GAW and ACTRIS stations. *Atmospheric Chemistry and Physics Discussions*, 12, 20849-20899 [(d)]

Overview: Trend analysis of number concentrations. Some traits seemed to be obvious: The global trends of particle number concentrations seem to be decreasing since the middle 1990s on; The trends of and N are relatively consistent in Northern Europe, but no clear similarity with optical properties trends were visible in the stations where all properties were measured;

Author contribution: I coded the GLS/ARB trend fitting routine based on literature algorithms, selected the data models and for a small part took a part in the MK method coding. I collected and checked the dataset, communicated with the data providers, did the data analysis and trend fitting, selected and collected the comparison datasets and did the related data analysis on them. I also wrote the paper, and collated the co-author comments and revisions. *Note that some of the figures have been enlarged from the ACPD version for better visibility in the thesis format.*

PV Makkonen., R, **Asmi, A.**, Kerminen, V.-M., Boy, M., Arneth, A., Hari, P., and Kulmala, M (2012). Air pollution control and decreasing new particle formation lead to strong climate warming. *Atmospheric Chemistry and Physics*, 12(3):1515-1524 [(d)]

Overview: We tested the effect of emission changes and new particle formation on anthropogenic aerosol forcing in present-day (year 2000) and future (year 2100) conditions. The predicted reduction in SO_2 emission rates will decrease the aerosol cooling effect, with potentially serious consequences, an effect even further increased by including current nucleation parametrizations in the model. Even including two climate feedbacks, radical increase in marine DMS or BVOC emissions in the future are not enough to overcome the SO_2 effect.

Author contribution: I contributed to the planning of the study, data interpretation and conclusions, choosing the simulations to be done, draw some of the figures, and participated on the writing of the paper.

BIBLIOGRAPHY

Ångström, A. (1929) On the atmospheric transmission of sun radiation and on dust in the air. *Geografiska Annaler*, 11:156–166.

Ackerman, A. S., *et al.* (2004) The impact of humidity above stratiform clouds on indirect aerosol climate forcing. *Nature*, 432(7020):1014–1017.

Aitken, J. (1889a) On improvements in the apparatus for counting the dust particles in the atmosphere. *Nature*, XXXIX.

Aitken, J. (1889b) On the number of dust particles in the atmosphere of certain places in Great Britain and on the continent, with remarks on the relation between the amount of dust and meteorological phenomena, part I. *Nature*, XLI.

Albrecht, B. A. (1989) Aerosol, cloud microphysics, and fractional cloudiness. *Science*, 245:1227–1230.

Andreae, M. and Rosenfeld, D. (2008) Aerosol-cloud-precipitation interactions. part 1. the nature and sources of cloud-active aerosols. *Earth-Sci. Rev.*, 89(1-2):13 – 41. doi:DOI: 10.1016/j.earscirev.2008.03.001.

Andreae, M., *et al.* (2005) Strong present-day cooling implies a hot future. *Nature*, 435:1187–1190.

Andreae, M. O. and Gelencsér, A. (2006) Black carbon or brown carbon? the nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys.*, 6(10):3131–3148. doi:10.5194/acp-6-3131-2006.

Anttila, T. and Kerminen, V.-M. (2003) Condensational growth of atmospheric nuclei by organic vapours. *Aerosol Sci.*, 34:41–61.

Arneth, A., *et al.* (2009) Clean the air, heat the planet? *Science*, 326(5953):672–673. doi: 10.1126/science.1181568.

Barmet, P., *et al.* (2009) Weekly cycle in particulate matter versus weekly cycle in precipitation over Switzerland. *J. Geophys. Res.*, 114:D05206. doi:10.1029/2008JD011192.

Bell, M. L., *et al.* (2004) A retrospective assessment of mortality from the London smog episode of 1952: The role of influenza and pollution. *Environ. Health Perspect.*, 112(1):6–8.

Bell, T. L. and Rosenfeld, D. (2008) Comment on "weekly precipitation cycles? lack of evidence from United States surface stations"; by D. M. Schultz et al. *Geophys. Res. Lett.*, 35(9):L09803.

Bergman, T., *et al.* (2012) Evaluation of the sectional aerosol microphysics module SALSA implementation in ECHAM5-HAM aerosol-climate model. *Geosci. Model Dev.*, 5(3):845–868. doi: 10.5194/gmd-5-845-2012.

Bonn, B., *et al.* (2008) How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation. *J. Geophys. Res.*, 113(D12):D12209.

Brasseur, G. P. and Roeckner, E. (2005) Impact of improved air quality on the future evolution of climate. *Geophys. Res. Lett.*, 32(23):L23704–.

Brimblecombe, P. (1987) *The Big Smoke: a history of air pollution in London since medieval times*. Methuen & Co. Ltd, London, UK. ISBN 0-416-90080-1.

Carslaw, K. S., *et al.* (2010) A review of natural aerosol interactions and feedbacks within the earth system. *Atmos. Chem. Phys.*, 10(4):1701–1737. doi:10.5194/acp-10-1701-2010.

Charlson, R. J., *et al.* (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albeno and climate. *Nature*, 326:655–661.

Chen, Y.-C., *et al.* (2011) A comprehensive numerical study of aerosol-cloud-precipitation interactions in marine stratocumulus. *Atmos. Chem. Phys.*, 11(18):9749–9769. doi:10.5194/acp-11-9749-2011.

Cofala, J., *et al.* (2007) Scenarios of global anthropogenic emissions of air pollutants and methane until 2030. *Atmos. Env.*, 41:8387–8499.

Collaud Coen, M., *et al.* (2012) Aerosol decadal trends – part 1: In-situ optical measurements at GAW and IMPROVE stations. *Atmos. Chem. Phys. Discuss.*, 12(8):20785–20848. doi: 10.5194/acpd-12-20785-2012.

Curry, J. A. and Khvorostyanov, V. I. (2012) Assessment of some parameterizations of heterogeneous ice nucleation in cloud and climate models. *Atmos. Chem. Phys.*, 12(2):1151–1172. doi: 10.5194/acp-12-1151-2012.

Daniel, J. S., *et al.* (2012) Identifying weekly cycles in meteorological variables: The importance of an appropriate statistical analysis. *J. Geophys. Res.*, 117(D13):D13203–.

Decesari, S., *et al.* (2000) Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach. *J. Geophys. Res.*, 105(D1):1481–1489.

Dockery, D. W. and Pope, C. (1994) Acute respiratory effects of particulate air pollution. *Annu. Rev. Public. Health*, 15:107–132.

Dockery, D. W., *et al.* (1993) An association between air polution and mortality in six U.S. cities. *N. Engl. J. Med.*, 329:1753–1749.

Donahue, N. M., *et al.* (2006) Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.*, 40:2635–2643. doi:10.1021/es052297c.

Donahue, N. M., *et al.* (2012) A two-dimensional volatility basis set part 2: Diagnostics of organic-aerosol evolution. *Atmos. Chem. Phys.*, 12(2):615–634. doi:10.5194/acp-12-615-2012.

Donaldson, K., *et al.* (1998) Ultrafine (nanometre) particle mediated lung injury. *J. Aerosol Sci.*, 29(5-6):553 – 560. doi:DOI: 10.1016/S0021-8502(97)00464-3.

Donaldson, K., *et al.* (2002) The pulmonary toxicology of ultrafine particles. *J. Aerosol Med.*, 15(2):213–220. doi: 10.1089/089426802320282338.

Dusek, U., *et al.* (2006) Size matters more than chemistry for cloud-nucleating ability of aerosol particles. *Science*, 312:1375–1378.

EC (2008) Commission regulation (EC) no 682/2008 of 18 july 2008. *Off. J. Eur. Union: Legis.*, L199:1–136. The Commission of the European Communities.

EC (2011) Commission staff working paper – summary of the impact assesment. accompanying document to the proposal for a directive of the european parliament and of the council amending directive 1999/32/ec as regards the sulphur content of marine fuels. Tech. Rep. SEC(2011) 919 final, European Commission, Brussels.

EEA (2012) *Air Quality in Europe – 2012 report.* No. 4/2012 in EEA Report. European Environment Agency, Copenhagen, 2012.

EMEP (2011) Transboundary particulate matter in Europe, joint CCC, MSC-W, CEIP and CIAM report 2011. Tech. rep., Convention on long-range transboundary air pollution, EMEP Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe., Kjeller, Norway. ISSN: 1504-6192.

Ervens, B., *et al.* (2010) CCN predictions using simplified assumptions of organic aerosol composition and mixing state: a synthesis from six different locations. *Atmos. Chem. Phys.*, 10(10):4795–4807. doi:10.5194/acp-10-4795-2010.

Ervens, B., *et al.* (2011) Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. *Atmos. Chem. Phys.*, 11(21):11069–11102. doi:10.5194/acp-11-11069-2011.

Facchini, M., *et al.* (1999) Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature*, 401:257–259.

Flossmann, A. I. and Wobrock, W. (2010) A review of our understanding of the aerosol–cloud interaction from the perspective of a bin resolved cloud scale modelling. *Atmos. Res.*, 97:478–497.

Forster, P. M. d. F. and Solomon, S. (2003) Observations of a weekend effect in diurnal temperature range. *Proc. Natl. Acad. Sci. U. S. A.*, 100(20):11225–11230. doi: 10.1073/pnas.2034034100.

Fountoukis, C., *et al.* (2012) Simulating ultrafine particle formation in Europe using a regional CTM: contribution of primary emissions versus secondary formation to aerosol number concentrations. *Atmos. Chem. Phys.*, 12(18):8663–8677. doi:10.5194/acp-12-8663-2012.

Fuzzi, S., *et al.* (2006) Critical assesment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. *Atmos. Chem. Phys.*, 6:2017–2038.

Ghan, S. J., *et al.* (2011) Droplet nucleation: Physically-based parameterizations and comparative evaluation. *J. Adv. Model. Earth Syst.*, 3:M10001. doi:10.1029/2011MS000074.

Gilman, D., *et al.* (1963) On the power spectrum of "red noise". *J. Atmos. Sci.*, 20:181–184.

Grönholm, T., *et al.* (2007) Measurements of aerosol particle dry deposition velocity using the relaxed eddy accumulation technique. *Tellus B*, 59(3):381–386. doi:10.1111/j.1600-0889.2007.00268.x.

Gultepe, I. and Isaac, G. A. (1999) Scale effects on averaging of cloud droplet and aerosol number concentrations: Observations and models. *J. Climate*, 12(5):1268–1279. doi:10.1175/1520-0442(1999)012¡1268:SEOAOC¿2.0.CO;2.

Gultepe, I., *et al.* (1996) Parameterizations of marine stratus microphysics based on in situ observations: Implications for GCMS. *J. Climate*, 9:345–357. doi:10.1175/1520-0442(1996)009¡0345:POMSMB¿2.0.CO;2.

Hand, J. L., *et al.* (2011) IMPROVE, spatial and seasonal patterns and temporal variability of haze and its constituents in the United States. Web report. Http://vista.cira.colostate.edu/improve/publications/Reports/2011/2011.htm, ISSN: 0737–5352–87.

Hansen, J., *et al.* (1981) Climate impact of increasing atmospheric carbon dioxide. *Science*, 213:4511.

Hanson, D. R. and Lovejoy, E. R. (2006) Measurement of the thermodynamics of the hydrated dimer and trimer of sulfuric acid. *J. Phys. Chem.*, 110:9525–9528.

Heintzenberg, J., *et al.* (1998) Mass-related aerosol properties over the Leipzig basin. *Journal of Geophysical Research D*, 103:13125–13135.

Heyder, J., *et al.* (2009) Long-term responses of canine lungs to acidic particles responses to acidic particles. *Inhal. Toxicol.*, 21(11):920–932.

Hirsch, R. M., *et al.* (1982) Techniques of trend analysis for monthly water quality data. *Water Resour. Res.*, 18(1):107–121.

Hoppel, W. A., *et al.* (1990) Aerosol size distributions and optical properties found in the marine boundary layer in the Atlantic ocean. *Journal of Geophysical Research D*, 95:3659–3686.

Iversen, T., *et al.* (2010) Assessing impacts of aerosol processes on equilibrium climate sensitivity. In Steyn, D. G. and Rao, S. T., eds., *Air Pollution Modeling and Its Application XX*, chap. Interactions between air quality and climate change, pp. 493–497. Springer.

Jaenicke, R. (2008) Is atmospheric aerosol an aerosol?–a look at sources and variability. *Faraday Discuss.*, 137:235–243. doi:10.1039/B701095H.

Jimenez, J. L., *et al.* (2009) Evolution of organic aerosols in the atmosphere. *Science*, 326(5959):1525–1529. doi:10.1126/science.1180353.

Junker, C., *et al.* (2006) Aerosol light absorption in the north atlantic: trends and seasonal characteristics during the period 1989 to 2003. *Atmos. Chem. Phys.*, 6(7):1913–1925. doi:10.5194/acp-6-1913-2006.

Kanakidou, M., *et al.* (2005) Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.*, 5(4):1053–1123. doi:10.5194/acp-5-1053-2005.

Kerminen, V. M. and Kulmala, M. (2002) Analytical formulae connecting the "real" and the "apparent" nucleation rate and the nuclei number concentration for atmospheric nucleation events. *J. of Aerosol Science*, 33:609–622.

Kerminen, V.-M. and Wexler, A. S. (1995) Enhanced formation and development of sulfate particles due to marine boundary layer circulation. *J. Geophys. Res.*, 100:23,051–23,062.

Kerminen, V. M., *et al.* (2000) Secondary organics and atmospheric cloud condensation nuclei production. *J. Geophys. Res.*, 105:9255–9264.

Kerminen, V.-M., *et al.* (2012) Cloud condensation nuclei production associated with atmospheric nucleation: a synthesis based on existing literature and new results. *Atmos. Chem. Phys. Discuss.*, 12(8):22139–22198. doi:10.5194/acpd-12-22139-2012.

Kim, K.-Y., *et al.* (2010) Weekend effect: Anthropogenic or natural? *Geophys. Res. Lett.*, 37(L09808). doi:10.1029/2010GL04323.

Kirkby, J., *et al.* (2011) Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476(7361):429–433.

Kloster, S., *et al.* (2008) Influence of future air pollution mitigation strategies on total aerosol radiative forcing. *Atmos. Chem. Phys.*, 8(21):6405–6437. doi:10.5194/acp-8-6405-2008.

Kloster, S., *et al.* (2010) A GCM study of future climate response to aerosol pollution reductions. *Climate Dyn.*, 34:1177–1194. 10.1007/s00382-009-0573-0.

Knight, C. G., *et al.* (2007) Association of parameter, software, and hardware variation with large-scale behavior across 57,000 climate models. *Proc. Natl. Acad. Sci. U. S. A.*, 104(30):12259–12264. doi:10.1073/pnas.0608144104.

Knote, C., *et al.* (2011) Towards an online-coupled chemistry-climate model: evaluation of trace gases and aerosols in cosmo-art. *Geosci. Model Dev.*, 4(4):1077–1102. doi:10.5194/gmd-4-1077-2011.

Koch, D. and Del Genio, A. D. (2010) Black carbon semi-direct effects on cloud cover: review and synthesis. *Atmos. Chem. Phys.*, 10(16):7685–7696. doi:10.5194/acp-10-7685-2010.

Konwar, M., *et al.* (2012) Aerosol control on depth of warm rain in convective clouds. *J. Geophys. Res.*, 117(D13):D13204.

Kroll, J. H., *et al.* (2011) Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat Chem*, 3(2):133–139.

Kuang, C., *et al.* (2008) Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations. *J. Geophys. Res.*, 113(D10):D10209–.

Kulmala, M., *et al.* (2004a) Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.*, 35:143–176.

Kulmala, M., *et al.* (2004b) Initial steps of aerosol growth. *Atmos. Chem. Phys.*, 4:2553–2560.

Kulmala, M., *et al.* (2004c) A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.*, 4:557–562.

Kulmala, M., *et al.* (2004d) Organic aerosol formation via sulphate cluster activation. *J. Geophys. Res.*, 109:10.1029/2003JD003961.

Kulmala, M., *et al.* (2011) General overview: European integrated project on aerosol cloud climate and air quality interactions (EUCAARI); integrating aerosol research from nano to global scales. *Atmos. Chem. Phys.*, 11(24):13061–13143. doi:10.5194/acp-11-13061-2011.

Kumar, P. and Foufoula-Georgiou, E. (1997) Wavelet analysis for geophysical applications. *Rev. Geophys.*, 35(4):385–412. doi:10.1029/97RG00427.

Kurtén, T., *et al.* (2008) Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia. *Atmos. Chem. Phys.*, 8(14):4095–4103. doi:10.5194/acp-8-4095-2008.

Laakso, L., *et al.* (2003) Ultrafine particle scavenging coefficients calculated from 6 years field measurements. *Atmos. Environ.*, 37:3605–3613.

Lack, D. A., *et al.* (2004) Seasonal variability of secondary organic aerosol: A global modeling study. *J. Geophys. Res.*, 109:doi:10.1029/2003JD00.

Lamarque, J.-F., *et al.* (2011) Global and regional evolution of short-lived radiatively-active gases and aerosols in the representative concentration pathways. *Clim. Change*, 109:191–212. doi:10.1007/s10584-011-0155-0.

Lee, L. A., *et al.* (2012) Mapping the uncertainty in global CCN using emulation. *Atmos. Chem. Phys. Discuss.*, 12(6):14089–14114. doi:10.5194/acpd-12-14089-2012.

Leibensperger, E. M., *et al.* (2012) Climatic effects of 1950–2050 changes in us anthropogenic aerosols – part 1: Aerosol trends and radiative forcing. *Atmos. Chem. Phys.*, 12(7):3333–3348. doi:10.5194/acp-12-3333-2012.

Lide, D. R. (2004) *CRC Handbook of Chemistry and Physics*. CRC Press LLC, 85th edn.

Lin, H. and Leaitch, W. R. (1997) Development of an in-cloud aerosol activation parameterization for climate modelling. In *Proceedings of the WMO Workshop on Measurement of Cloud Properties for Forecasts of Weather, Air Quality and Climate*, pp. 328–335. World Meteorol. Organ, Geneva.

Liu, B. Y. H. and Kim, C. S. (1977) On the counting efficiency of condensation nuclei counters. *Atmos. Environ.*, 11:1097–1100.

Lohmann, U., *et al.* (2007) Cloud microphysics and aerosol indirect effects in the global climate model ECHAM5-HAM. *Atmos. Chem. Phys.*, 7(13):3425–3446.

Lohmann, U., *et al.* (2010) Total aerosol effect: radiative forcing or radiative flux perturbation? *Atmos. Chem. Phys.*, 10(7):3235–3246. doi:10.5194/acp-10-3235-2010.

Löndahl, J., *et al.* (2010) Aerosol exposure versus aerosol cooling of climate: what is the optimal emission reduction strategy for human health? *Atmos. Chem. Phys.*, 10(19):9441–9449. doi:10.5194/acp-10-9441-2010.

Lovejoy, E., *et al.* (2004) Atmospheric ion-induced nucleation of sulfuric acid and water. *J. Geophys. Res.*, 109:D08204.

Lu, M.-L. and Seinfeld, J. H. (2005) Study of the aerosol indirect effect by large-eddy simulation of marine stratocumulus. *J. Atmos. Sci.*, 62(11):3909–3932. doi:10.1175/JAS3584.1.

Makkonen, R., *et al.* (2012) Brightening of the global cloud field by nitric acid and the associated radiative forcing. *Atmos. Chem. Phys.*, 12(16):7625–7633. doi:10.5194/acp-12-7625-2012.

Mann, G. W., *et al.* (2012) Intercomparison of modal and sectional aerosol microphysics representations within the same 3-d global chemical transport model. *Atmos. Chem. Phys.*, 12(10):4449–4476. doi:10.5194/acp-12-4449-2012.

Mårtensson, E. M., *et al.* (2003) Laboratory simulations and parameterization of the primary marine aerosol production. *J. Geophys. Res.*, 108(D9):4297–.

Martin, G. M., *et al.* (1994) The measurement and parameterization of effective radius of droplets in warm stratocumulus clouds. *J. Atmos. Sci*, 51:18231842. doi:10.1175/1520-0469(1994)051¡1823:TMAPOE¿2.0.CO;2.

Mauldin III, R. L., *et al.* (2012) A new atmospherically relevant oxidant of sulphur dioxide. *Nature*, 488(7410):193–196.

McFiggans, G., *et al.* (2006) The effect of physical and chemical aerosol properties on warm cloud droplet activation. *Atmos. Chem. Phys.*, 6(9):2593–2649. doi:10.5194/acp-6-2593-2006.

McFiggans, G., *et al.* (2010) The sensitivity of secondary organic aerosol component partitioning to the predictions of component properties part 1: A systematic evaluation of some available estimation techniques. *Atmos. Chem. Phys.*, 10(21):10255–10272. doi:10.5194/acp-10-10255-2010.

McMichael, A. J., *et al.* (2006) Climate change and human health: present and future risks. *Lancet*, 367(9513):859–869.

McMurry, P. (2000) A review of atmospheric aerosol measurements. *Atmos. Environ.*, 34:1959–1999.

McMurry, P., *et al.* (2005) A criterion for new particle formation in the sulfur-rich Atlanta atmosphere. *J. Geophys. Res.*, 110:Art. No. D22S02.

Merikanto, J., *et al.* (2009) Impact of nucleation on global CCN. *Atmos. Chem. Phys.*, 9(21):8601–8616. doi:10.5194/acp-9-8601-2009.

Mohnen, V. and Hidy, G. M. (2010) Measurements of atmospheric nanoparticles (1875–1980). *Bull. Amer. Meteor. Soc.*, 91(11):1525–1539. doi:10.1175/2010BAMS2929.1.

Nakicenovic, N., *et al.* (2000) *Special Report on Emissions Scenarios (SRES)*. IPCC reports. Cambridge University Press, UK.

Napari, I., *et al.* (2002) Ternary nucleation of inorganic acids, ammonia, and water. *J. Chem. Phys*, 117:8418–8425.

Nenes, A., *et al.* (2001) A theoretical analysis of cloud condensation nucleus (CCN) instruments. *J. Geophys. Res.*, 106(D4):3449–3474.

Nieminen, T., *et al.* (2009) Connection of sulfuric acid to atmospheric nucleation in boreal forest. *Environ. Sci. Technol.*, 43(13):4715–4721. doi:10.1021/es803152j.

Nilsson, E., *et al.* (2001) Turbulent aerosol fluxes over the Arctic Ocean 2. wind-driven sources from the sea. *J. of Geophys Res.*, 106:32139–32154.

Oberdörster, G., *et al.* (2005) Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles. *Environ. Health Perspect.*, 113(7). doi:doi:10.1289/ehp.7339.

O'Donnell, D., *et al.* (2011) Estimating the direct and indirect effects of secondary organic aerosols using ECHAM5-HAM. *Atmos. Chem. Phys.*, 11(16):8635–8659. doi:10.5194/acp-11-8635-2011.

Odum, J., *et al.* (1997) Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. *Environ. Sci. Technol.*, 31:1890–1897.

Paasonen, P., *et al.* (2010) On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation. *Atmos. Chem. Phys.*, 10(22):11223–11242. doi:10.5194/acp-10-11223-2010.

Paasonen, P., *et al.* (2012) On the formation of sulphuric acid-amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation. *Atmos. Chem. Phys. Discuss.*, 12(5):11485–11537. doi:10.5194/acpd-12-11485-2012.

Petters, M. D. and Kreidenweis, S. M. (2007) A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.*, 7(8):1961–1971. doi:10.5194/acp-7-1961-2007.

Pierce, J. R. and Adams, P. J. (2007) Efficiency of cloud condensation nuclei formation from ultrafine particles. *Atmos. Chem. Phys.*, 7(5):1367–1379. doi:10.5194/acp-7-1367-2007.

Pope, C. A. I. (2000) Review: Epidemiological basis for particulate air pollution health standards. *Aerosol Sci. Technol.*, 32:4–14.

Prisle, N. L., *et al.* (2012) Surfactant effects in global simulations of cloud droplet activation. *Geophys. Res. Lett.*, 39(5):L05802–.

Pruppacher, H. and Klett, J. (1997) *Microphysics of Clouds and Precipitation*. Kluwer Academic Publishers, second revised and enlarged edn.

Pryde, J., *et al.* (2011) Sensory and chemical analysis of 'Shackletons' Mackinlay scotch whisky. *J. Inst. Brew.*, 117:156–165.

Pryor, S. C., *et al.* (2008) A review of measurement and modelling results of particle atmosphere–surface exchange. *Tellus B*, 60(1):42–75. doi: 10.1111/j.1600-0889.2007.00298.x.

Putaud, J.-P., *et al.* (2004) A European aerosol phenomenology - 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ.*, 38:2579–2995.

Raes, F., *et al.* (2000) Formation and cycling of aerosols in the global troposhere. *Atmos. Environ.*, 34:4215–4240.

Ramanathan, V., *et al.* (2001a) Aerosols, climate and the hydrological cycle. *Science*, 294:2119–2124.

Ramanathan, V., *et al.* (2001b) Indian Ocean Experiment: An integrated analysis of the climate forcing and effects of the great Indo-Asian haze. *J. Geophys. Res.*, 106(D22):28371–28398. doi: 10.1029/2001JD900133.

Ramanathan, V., *et al.* (2005) Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle. *Proc. Natl. Acad. Sci. U. S. A.*, 102(15):5326–5333. doi: 10.1073/pnas.0500656102.

Ramaswamy, V., *et al.* (2001) *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, chap. Radiative forcing of climate change, pp. 349–416. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Reddington, C. L., *et al.* (2011) Primary versus secondary contributions to particle number concentrations in the European boundary layer. *Atmos. Chem. Phys.*, 11(23):12007–12036. doi: 10.5194/acp-11-12007-2011.

Riemer, N., *et al.* (2010) Estimating black carbon aging time-scales with a particle-resolved aerosol model. *J. Aerosol Sci.*, 41(1):143 – 158. doi: 10.1016/j.jaerosci.2009.08.009.

Riipinen, I., *et al.* (2012) The contribution of organics to atmospheric nanoparticle growth. *Nature Geosci.*, 5(7):453–458.

Robinson, A. L., *et al.* (2007) Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science*, 315(5816):1259–1262. doi: 10.1126/science.1133061.

Robock, A. (2008) 20 reasons why geoengineering may be a bad idea. *Bulletin of the Atomic Scientists*, 64(14):14–18. doi:10.2968/064002006.

Roeckner, E., *et al.* (2003) The atmospheric general circulation model ECHAM5. PART I: Model description. *MPI-Report*, 349:127 pp.

Sager, T. and Castranova, V. (2009) Surface area of particle administered versus mass in determining the pulmonary toxicity of ultrafine and fine carbon black: comparison to ultrafine titanium dioxide. *Part. Fibre Toxicol.*, 6(1):15. doi: 10.1186/1743-8977-6-15.

Sanchez-Lorenzo, A., *et al.* (2012) Assessing large-scale weekly cycles in meteorological variables: a review. *Atmos. Chem. Phys.*, 12(13):5755–5771. doi:10.5194/acp-12-5755-2012.

Seinfeld, J. and Pandis, S. (2006) *Atmospheric chemistry and physics: From air pollution to climate change*. Wiley Interscience, 2nd edn.

Sen, P. K. (1968) Esimates of the regression coefficient based on Kendall's tau. *J. Am. Statist. Assoc.*, 63(324):1379–1389.

Shepherd, J., *et al.* (2009) *Geoengineering the climate: science, governance and uncertainty*. RS Policy document. The Royal Society, London, UK.

Sihto, S.-L., *et al.* (2006) Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms. *Atmos. Chem. Phys.*, 6:4079–4091.

Sihto, S.-L., *et al.* (2011) Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest. *Atmos. Chem. Phys.*, 11(24):13269–13285. doi:10.5194/acp-11-13269-2011.

Sipilä, M., *et al.* (2010) The role of sulfuric acid in atmospheric nucleation. *Science*, 327(5970):1243–1246. doi: 10.1126/science.1180315.

Smith, S. J., *et al.* (2004) Historical sulfur dioxide emissions 1850–2000: Methods and results. PNNL Research Report PNNL-14537, Pacific Northwest National Laboratory, Joint Global Change Research Institute, 8400 Baltimore Avenue, College Park, Maryland 20740.

Smith, S. J., *et al.* (2011) Anthropogenic sulfur dioxide emissions: 1850–2005. *Atmos. Chem. Phys.*, 11(3):1101–1116. doi:10.5194/acp-11-1101-2011.

Spracklen, D. V., *et al.* (2006) The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales. *Atmos. Chem. Phys.*, 6(12):5631–5648. doi:10.5194/acp-6-5631-2006.

Spracklen, D. V., *et al.* (2010) Explaining global surface aerosol number concentrations in terms of primary emissions and particle formation. *Atmos. Chem. Phys.*, 10(10):4775–4793. doi:10.5194/acp-10-4775-2010.

Stier, P., *et al.* (2005) The aerosol-climate model ECHAM5-HAM. *Atmos. Chem. Phys.*, 5:1125–1156.

Struthers, H., *et al.* (2011) The effect of sea ice loss on sea salt aerosol concentrations and the radiative balance in the Arctic. *Atmos. Chem. Phys.*, 11(7):3459–3477.

Su, H., *et al.* (2011) Soil nitrite as a source of atmospheric HONO and OH radicals. *Science*, 333(6049):1616–1618. doi:10.1126/science.1207687.

Textor, C., *et al.* (2007) The effect of harmonized emissions on aerosol properties in global models an AeroCom experiment. *Atmos. Chem. Phys.*, 7(17):4489–4501. doi:10.5194/acp-7-4489-2007.

Torrence, C. and Compo, P. (1998) A practical guide to wavelet analysis. *Bull. Am. Meteorol. Soc.*, 79:61–78.

Tost, H. and Pringle, K. J. (2012) Improvements of organic aerosol representations and their effects in large-scale atmospheric models. *Atmos. Chem. Phys.*, 12(18):8687–8709. doi:10.5194/acp-12-8687-2012.

Tsigaridis, K. and Kanakidou, M. (2003) Global modelling of secondary organic aerosol in the troposphere: sensitivity analysis. *Atm. Chem. Phys.*, 3:1849–1869.

Twomey, S. (1977) The influence of pollution on the shortwave albedo of clouds. *J. Atmos. Sci.*, 34:1149–1152.

van Dingenen, R., *et al.* (2004) A European aerosol phenomenology - I: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ.*, 38:2561–2577.

van Vuuren, D. P., *et al.* (2011) The representative concentration pathways: an overview. *Clim. Change*, 109:5–31. doi:10.1007/s10584-011-0148-z.

Vanhanen, J., *et al.* (2011) Particle size magnifier for nano-CN detection. *Aerosol Sci. Tech.*, 45(4):533–542.

Vehkamäki, H., *et al.* (2002) An improved parameterization for sulfuric acid/water nucleation rates for tropospheric and stratospheric conditions. *J. Geophys. Res.*, 107:4622–4631.

Vignati, E., *et al.* (2004) M7: An efficient size-resolved aerosol microphysics module for large-scale aerosol transport models. *J. Geophys. Res.*, 109(D22202). doi:10.1029/2003JD004485.

Virkkula, A., *et al.* (2011) Seasonal cycle, size dependencies, and source analyses of aerosol optical properties at the SMEAR II measurement station in Hyytiälä, Finland. *Atmos. Chem. Phys.*, 11(9):4445–4468. doi:10.5194/acp-11-4445-2011.

Wang, J., *et al.* (2008) Sensitivity of sulfate direct climate forcing to the hysteresis of particle phase transitions. *J. Geophys. Res.*, 113(D11):D11207.

Wang, S., *et al.* (2003) Turbulence, condensation, and liquid water transport in numerically simulated nonprecipitating stratocumulus clouds. *J. Atmos. Sci.*, 60(2):262–278. doi:10.1175/1520-0469(2003)060¡0262:TCALWT¿2.0.CO;2.

Wang, X. L. and Swail, V. (2001) Changes of extreme wave heights in northern hemisphere oceans and related atmospheric circulation regimes. *J. Climate*, 14:2204–2221.

Weber, R. J., *et al.* (1996) Measured atmospheric new particle formation rates: implications for nucleation mechanisms. *Chem. Eng. Comm*, 151:53–64.

Wiedensohler, A., *et al.* (2012) Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions. *Atmos. Meas. Tech.*, 5(3):657–685. doi:10.5194/amt-5-657-2012.

Wilks, D. S. (1997) Resampling hypothesis tests for autocorrelated fields. *J. Climate*, 10:65–81.

Wittmaack, K. (2007) In search of the most relevant parameter for quantifying lung inflammatory response to nanoparticle exposure: Particle number, surface area, or what? *Environ. Health Perspect.*, 115(2). doi:doi:10.1289/ehp.8871.

Yin, Y., *et al.* (2002) Interactions of mineral dust particles and clouds: Effects on precipitation and cloud optical properties. *J. Geophys. Res.*, 107(D23):4724–.

Yli-Juuti, T., *et al.* (2011) Growth rates of nucleation mode particles in Hyytiälä during 2003-2009: variation with particle size, season, data analysis method and ambient conditions. *Atmos. Chem. Phys.*, 11(24):12865–12886. doi: 10.5194/acp-11-12865-2011.

Yu, F. and Turco, R. P. (2000) Ultrafine aerosol formation via ion-mediated nucleation. *Geophys. Res. Lett.*, 27:883–886.

Zábori, J., *et al.* (2012a) Artificial primary marine aerosol production: a laboratory study with varying water temperature, salinity, and succinic acid concentration. *Atmos. Chem. Phys.*, 12(22):10709–10724.

Zábori, J., *et al.* (2012b) Wintertime Arctic Ocean sea water properties and primary marine aerosol concentrations. *Atmos. Chem. Phys.*, 12:10405–10421. doi:10.5194/acp-12-10405-2012.